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SOCIETY OF DYERS
AND COLOURISTS

CONTENTS

Proceedings of the Society

Report of the Committee on the Dyeing Properties of Vat Dyes

Introduction

The Committee was appointed by Council in March 1948 with the object of standardising a series of tests which would provide the more essential information required about the dyeing properties of vat dyes. The Committee, the constitution of which is given in Appendix I, held thirteen meetings between May 1948 and February 1950.

The first and obvious requirement was a knowledge of the conditions which provided maximum colour yield. The Committee therefore surveyed the methods recommended by the principal dye manufacturers. It was evident that there was good agreement on the methods to be employed for the accepted classes of vat dyes.

Considering, in the first place, only the anthraquinonoid dyes, the Committee chose three dyeing methods based on those of the dye manufacturers, viz. the strong alkali, the weak alkali–high temperature, and the weak alkali–low temperature methods. They also examined a method which was intermediate between the first two. The dyeings obtained by these methods were used to determine the conditions of maximum colour yield. Details were laid down for the procedure to be followed in vatting, dyeing, and finishing.

Members then dyed six vat dyes according to each of the four methods. The resulting dyeings, when assessed on the basis of the maximum colour yield, confirmed the makers' recommendations for the three most suitable dyeing methods. There appeared to be little scope for the introduction of the intermediate method, but a decision was deferred until the dyeing of mixtures had been considered. The Committee adopted the three dyeing methods, with minor changes, as Methods I, II, and III.

The influence of salt and temperature on colour yield was also investigated. The influence of these factors was not great, and did not warrant additional tests, since the conditions obtaining in one of the prescribed dyeing tests usually coincided with the optimum conditions of salt and temperature. Higher temperatures were liable to effect changes in the hue of the dyeing.

Details were laid down for the yarn on which tests were to be carried out, and in all their subsequent work the Committee members used the same supply of yarn in order to avoid any possible variation from this source.

The method which gave optimum colour yield having been determined, further information was required on the level-dyeing properties of a dye. The following tests were suggested for this purpose—

A MIGRATION TEST— A dyed hank and a white hank are entered together into a blank dyebath (i.e. omitting the dye) and treated together for, say, 40 min. Comparison of the depths of dyeing on the two hanks then affords a measure of the migrating capacity of the dye.

A STRIKE–LEVELLING TEST— A hank is entered into a dyebath and followed by a second hank after, say, 2 min. Dyeing is then continued for, say, 40 min., after which the depths of dyeing on the two hanks are compared.

The results obtained by both these tests were found to depend to a large extent on the depth of dyeing. A suitable depth for showing the differences between dyes was therefore chosen, and laid down in the specification.

The Strike–Levelling Test, which combines the effects of rate of dyeing and migration, was found to give results which corresponded well with the known dyeing behaviour of the dyes tested.

The Migration Test, which compares the intrinsic levelling capacities of dyes when tested under strictly comparable conditions, was considered to provide information on the ease with which an initially unlevel material could be levelled and especially on the influence of temperature on this property. This test was therefore prescribed to be carried out at two temperatures, a normal dyeing temperature and an elevated temperature, a note being made of any change in hue at the higher temperature. A few vat dyes may be partly destroyed at the higher temperature without this being obvious visually.

The Committee were aware at this stage of the proposal of the Committee on the Dyeing Properties of Wool Dyes to use a scale of contrasts made from grey dyeings (subsequently known as the S.D.C. Grey Scale No. 2) for assessing the results of migration tests[1]. When members of the present committee used this scale for assessing the results

of the Strike–Levelling and Migration Tests, they obtained at first considerable differences in their assessments. This was found to be due mainly to differences in the manner of using the grey scale. There was a tendency to match the lighter of the pair of dyed yarns with the lighter portion of one of the pairs on the grey scale. It was also found that more consistent results were obtained when the dyeings were mounted in a standard manner on a black card. After more precise instructions had been formulated, more consistent assessments were obtained, and the Committee unanimously adopted the Grey Scale No. 2. The method of mounting referred to above was also accepted by the Committee. (For details see Appendix II.)

In order to detect any differences in experimental conditions in different laboratories, the Committee selected a dye which could be recommended as a standard and which should give a predetermined result in the Strike–Levelling and Migration Tests. Caledon Jade Green XN was chosen for this purpose, since it had given the most reproducible results in interlaboratory comparisons. The behaviour of this dye under the tests was therefore defined in terms of a number on the Grey Scale No. 2. Tests on this dye serve to calibrate the operator's method of test, and they should therefore be carried out prior to undertaking tests on other dyes.

The Committee then considered the indigoid class of dyes. It was found that the tests prescribed for the anthraquinonoid dyes were also suitable for the indigoid dyes when modified to give more information on the influence of vatting temperature.

The tests so far considered have been designed to assess the dyeing properties of individual vat dyes. In practice, since the dyes will often be used in mixtures, some further information may be required. The Committee considered that a rate-of-dyeing test would provide the most useful information. After preliminary tests on various mixtures, it was decided that the test should consist of three dyeings carried out for 2, 5, and 40 min. respectively. Differences in rate of dyeing are manifest as differences of hue in the dyeings. This test is qualitative in nature, and will presumably be carried out under conditions approaching those obtaining in bulk, usually according to two or more methods in order to determine which gives the most uniform rate of absorption. The differences in the results obtained when using dyeing Methods I and II were found to be sufficiently small to make it unnecessary to retain an intermediate method.

The results of the application of the recommended tests to a range of vat dyes in common use are given in Appendix III.

Tests were first made on the standard cotton yarn, but it was considered desirable to make comparative tests on mercerised cotton, viscose, and linen yarns. In general similar results were obtained on the different fibres, but there were a few differences, which may be important enough in practice to justify the separate testing of any particular material.

Recommended Methods of Test

1. MATERIALS USED

YARN— The tests are carried out on 40s/2 bleached American yarn having a medium doubling twist (about 15 t.p.in.) and having a fluidity value not exceeding 5 when measured in a standard cuprammonium solution[2].

WATER— Water not exceeding a hardness of 5 parts of calcium carbonate per 100,000 (3·5° hardness) is employed throughout.

DYES— Wherever possible powder brands are used. These are wetted with a little methylated spirit and then made into a suspension with water. Aliquot amounts are measured by pipette from the suspension as required. If the suspension is unsatisfactory, however, direct weighing of the dye for each dyebath is advisable. When paste brands are used, the same procedure is followed.

Indigoid dyes are pasted with Calsolene Oil HS (ICI) or a similar product at the rate of 0·5 ml. per gram of dye. The oil may be diluted to a 25% solution if desired.

2. DYEING TESTS

(a) Anthraquinonoid Dyes

DEPTH OF SHADE— Dyeings are made in full shades equivalent in strength to the following—

	Dyed by Method
20% Caledon Yellow 5GS Paste Fine ...	I
20% Caledon Brilliant Red 3BS Paste Fine...	II
4% Cibanone Red 4B Powder	II
20% Caledon Brilliant Violet RS Paste Fine ...	III
6% Caledon Brilliant Violet 3BS Paste Fine	I
20% Caledon Jade Green XNS Paste Fine ...	I
20% Caledon Blue RCS Paste Fine	I
20% Caledon Grey MS Paste Fine	I

LIQUOR RATIO— A liquor : goods ratio of 30 : 1 is used.

DYEING METHOD— Dyeings are carried out in tall beakers, and the hanks are worked on a bent rod so that the material is kept below the surface of the liquor. The vat is prepared with one-quarter of the volume of water required for the dyebath and approximately three-quarters of the stated quantities of caustic soda and sodium hydrosulphite. Vatting is allowed to proceed for 10 min. or until such time as a perfect solution is obtained.

The unused caustic soda and hydrosulphite are dissolved in the remaining water and then added to the vat. The hanks are thoroughly wetted in hot water only, cooled, squeezed so that they contain not more than their own weight of water, and entered into the dyebath. Where common salt is specified it should be in a finely ground condition and should be added to the dyebath in the solid state, 20 min. from the start of the dyeing. The hanks are turned for 1 min. in every 5 min.

TABLE I

Details for Dyeing 10 g. Yarn with Anthraquinonoid Dyes

Method	I	II	III
Caustic soda (53°Tw., i.e. 300 g./litre solution), ml.	4·5	2·0	2·0
Sodium hydrosulphite, g.	1·0	1·0	1·0
Common salt, g.	—	3·0	6·0
Vatting temperature, °C.	60	50	40
(°F.)	(140)	(120)	(105)
Dyeing temperature, °C.	60	50	20
(°F.)	(140)	(120)	(70)
Dyeing time, min.	40	40	40

The necessary details for vatting and dyeing by the three methods are given in Table I.

AFTERTREATMENT— The hanks after removal from the dyebath are treated as follows—

(i) Squeezed so that they contain about their own weight of liquor and allowed to oxidise completely in air.

(ii) Rinsed in cold running water.

(iii) Soured in sulphuric acid of concentration 0·5 ml. of 160° Tw. acid per litre for 5 min. at room temperature at a liquor ratio of 30 : 1.

(iv) Rinsed in cold running water.

(v) Treated in soap of concentration 2 g./litre for 10 min. at the boil at a liquor ratio of 30 : 1.

(vi) Rinsed, dried.

ASSESSMENT— The preferred dyeing method is that which gives the greatest colour yield; it is classed as Grade 5, and the results obtained by the other two methods are then given grades by assessing the differences from the preferred method in terms of the S.D.C. Grey Scale No. 2.

(b) Indigoid Dyes

DEPTH OF SHADE— Dyeings are made in full shades equivalent in strength to the following—

20% Durindone Red 3BS Paste ... Dyed by Method VI (vatted at 80°C.)

5% Ciba Blue 2B Powder ... ... Dyed by Method VI (vatted at 80°C.)

Where, however, a dye is normally used for pale shades only, it is tested at such a depth, e.g.—

5% Durindone Pink FFS Paste ... Dyed by Method VI (vatted at 80°C.)

LIQUOR RATIO— A liquor : goods ratio of 30 : 1 is used.

DYEING METHOD— The general procedure is the same as for the anthraquinonoid dyes, but vatting is carried out for 20 min. at two different temperatures. The necessary details for vatting and dyeing by the three methods are given in Table II.

TABLE II

Details for Dyeing 10 g. Yarn with Indigoid Dyes

Method					IV	V	VI
Caustic soda (53°Tw., i.e. 300 g./litre solution), ml.					4·5	2·0	2·0
Sodium hydrosulphite, g.		...	...		1·0	1·0	1·0
Common salt, g.		...	...	...	—	3·0	6·0
Vatting temperature—							
(i) °C.	...	...	...	...	50	50	50
(°F.)	...	...	...	...	(120)	(120)	(120)
(ii) °C.	...	...	...	...	80	80	80
(°F.)	...	...	...	...	(175)	(175)	(175)
Dyeing temperature, °C.	...	...	...	60	50	50
(°F.)	...	...	...	...	(140)	(120)	(120)
Dyeing time. min.	...	...	...	40	40	40

AFTERTREATMENT—As for the anthraquinonoid dyes.

ASSESSMENT— As for the anthraquinonoid dyes.

3. STRIKE–LEVELLING TEST

This test is designed to determine (A) the "strike" and (B) the ability of partly dyed material to level. For this purpose two separate dyebaths are used.

The amount of dye to be used in each dyebath is equivalent to the following—

	Dyed by Method
5% Caledon Yellow 5GS Paste Fine ...	I
1% Cibanone Red 4B Powder ...	II
5% Caledon Dark Brown 3RS Paste Fine ...	II
5% Caledon Jade Green XNS Paste Fine ...	I
5% Caledon Brilliant Violet RS Paste Fine ...	III
5% Caledon Blue RCS Paste Fine	I
20% Caledon Dark Blue BMS Paste Fine ...	I

The last dyeing is used as the standard depth for navy blues and blacks, but if it is required to assess these in lighter shades 5% Caledon Blue RCS is to be taken as the standard depth.

In the Strike–Levelling Test the quantities of caustic soda, sodium hydrosulphite, and water and also the vatting temperature are those which are used in the preferred dyeing method. The dyeing temperature is the same as in the preferred method, but Method III dyes are also tested at 50°C. (120°F.). No salt is added in any method.

(A) DETERMINATION OF STRIKE— A 5-g. hank is entered into the dyebath, and is turned steadily and continuously. After 2 min. a second 5-g. hank is entered, and both are turned in the same way. After a further 3 min. (i.e. after 5 min. from the start) both hanks are removed from the dyebath and aftertreated as described under DYEING TESTS. The difference in depth of shade between the two hanks is then assessed in terms of the S.D.C. Grey Scale No. 2.

(B) DETERMINATION OF LEVELLING— A 5-g. hank is entered into the dyebath, and is turned steadily and continuously. After 2 min. a second 5-g. hank is entered, and both are turned in the same way for 3 min. Thereafter the hanks are turned for 1 min. in every 5 min. After a further 35 min. (i.e. after 40 min. from the start) both hanks are removed from the dyebath and aftertreated as described under DYEING TESTS. The difference in depth of shade between the two hanks is then assessed in terms of the S.D.C. Grey Scale No. 2.

STANDARD FOR STRIKE–LEVELLING TEST— In order to assist in obtaining the correct conditions for carrying out this test, a preliminary test is made using 5% Caledon Jade Green XNS Paste Fine applied by Method I on the standard 40s/2 bleached cotton yarn. This dye should give the following results when assessed on the S.D.C. Grey Scale No. 2—

Strike	...	...	Grade 2–3
Levelling	...	...	Grade 3–4

NOTE— The influence of temperature on the degree of levelling may be determined by carrying out the test at different temperatures. The test may also be used for studying the influence of other aids to levelling, e.g. restraining agents.

4. MIGRATION TEST

This test is designed to determine the ease with which the dye on a dyed material can be transferred to undyed material.

The amount of dye to be used in making the dyeing is the same as prescribed for the Strike–Levelling Test.

The test is carried out at the two temperatures given in Table III.

TABLE III
Temperatures of Migration Test

Dyeing Method		Temperatures			
		°C.	(°F.)	°C.	(°F.)
I	...	50	(120)	80	(175)
II	...	50	(120)	80	(175)
III	...	20	(70)	50	(120)
IV	...	50	(120)	80	(175)
V	...	50	(120)	80	(175)
VI	...	50	(120)	80	(175)

No salt is added in any method.

DETERMINATION OF MIGRATION— Two 5-g. hanks are dyed by the preferred dyeing method as described under DYEING TESTS and aftertreated with the exception of soaping. One of the dyed hanks and a 5-g. undyed hank are placed in a bath containing the same amounts of caustic soda, sodium hydrosulphite, and water as are used in dyeing a 10-g. hank by the preferred dyeing method. The hanks are treated in the "blank" bath for 40 min., being turned steadily for the first 5 min. and thereafter for 1 min. in every 5 min. They are then removed from the bath and after-treated as described under DYEING TESTS, the second of the original two dyed hanks being included at the soaping stage. The difference in depth of shade between the two hanks which have been treated in the blank bath is then assessed in terms of the scale of contrasts given by the S.D.C. Grey Scale No. 2. Any change in hue of the dyed hank treated at 80°c. is noted.

STANDARD FOR MIGRATION TEST— In order to assist in obtaining the correct conditions for carrying out this test, a preliminary test is made using 5% Caledon Jade Green XNS Paste Fine applied by Method I on the standard 40s/2 bleached cotton yarn. This dye should give the following results when assessed on the S.D.C. Grey Scale No. 2—

At 50°c. ... ... Grade 1
At 80°c. ... ... Grade 3-4

5. RATE-OF-DYEING TEST FOR MIXTURES

This test is designed to determine the behaviour of a mixture of vat dyes when used to produce a compound shade. It may be applied at any depth of shade and by any dyeing method, with or without the addition of common salt or restraining agents. Normally the conditions of testing are those described under DYEING TESTS, but the dyer will obtain the most useful information by carrying out this test under conditions as near as possible to those under which the mixture will be used in practice.

METHOD OF TESTING— The mixture of dyes is dyed at the selected strength in separate dyebaths for (a) 2 min., (b) 5 min., (c) 40 min.

Unless decided otherwise, the conditions of dyeing and aftertreatment are the same as for DYEING TESTS.

ASSESSMENT— This is a qualitative test only. If the three dyeings obtained are of the same hue, then the mixture dyes satisfactorily under the conditions of the test; but if there is a large difference in hue between the three dyeings, then the mixture is unsatisfactory.

APPENDIX I
Constitution of the Committee

The organisations which co-operated in the work of the Committee are listed below—

ORGANISATION		REPRESENTATIVE
Allied Colloids Ltd.	...	Mr. R. Pendlebury
Henry Ashwell & Co. Ltd.	...	Mr. T. F. Heyes
Bradford Dyers' Association Ltd.	...	Mr. E. Wilson
British Cotton & Wool Dyers' Association Ltd.	...	Dr. P. W. Cunliffe
Clayton Aniline Co. Ltd.	...	Mr. F. W. Bradley
Courtaulds Ltd.	...	Mr. H. Hampson
English Sewing Cotton Co. Ltd.	...	Mr. E. B. Adams (the late)
Geigy Co. Ltd.	...	Mr. A. Goddard
L. B. Holliday & Co. Ltd.	...	Mr. M. R. Fox
		Mr. T. Minshall
		Mr. H. Haigh
Imperial Chemical Industries Ltd.	...	Mr. E. R. Wiltshire
Linen Industry Research Association	...	Mr. D. A. Derrett-Smith
Sandoz Products Ltd.	...	Mr. C. Holmes
Wm. Smith & Co. Ltd.	...	Mr. F. Smith
University of Leeds	...	Dr. C. B. Stevens
Yorkshire Dyeware & Chemical Co. Ltd.	...	Mr. A. Thomson

Mr. F. Ashworth also attended the meetings.

Minutes of the meetings were sent to the following for information—

The British Cotton Industry Research Association
Dr. S. M. Neale
Mr. F. Scholefield

Dr. P. W. Cunliffe was Chairman of the Committee and Mr. H. Hampson Vice-chairman. Mr. M. R. Fox was Honorary Secretary for the first four meetings, and thereafter Mr. E. R. Wiltshire.

APPENDIX II
Mounting of Patterns for Assessment

The following method of mounting is recommended by the Committee—

A portion of the hank is selected and laid on a piece of matt black cardboard, 1½ in. wide, as shown in Fig. 1. The thickness of the selected portion of hank is such that when flattened it gives
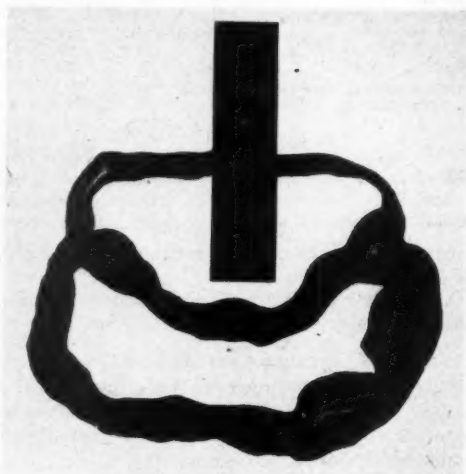
FIG. 1

a pad of threads about ½ in. wide. The yarn is cut at a distance of ½ in. from each side of the card, which is then reversed (Fig. 2). The ends of the pad of yarn are secured to the back of the card with adhesive tape (Fig. 3).

Samples which are to be compared are always mounted side by side, avoiding any gap between them. The three samples from the Dyeing Test are mounted together with the darkest in the middle so that it may be compared in turn with the other two. The samples from the Strike–Levelling Tests are mounted in pairs (Fig. 4). The samples from the Migration Test are likewise mounted in pairs, but it may be convenient to include the original dyeing on this card for reference purposes.

In carrying out the assessment the cards are held side by side with the Grey Scale No. 2 against a large black background. By these means it should be possible to estimate the degree of contrast between samples to within half a unit on the grey scale.
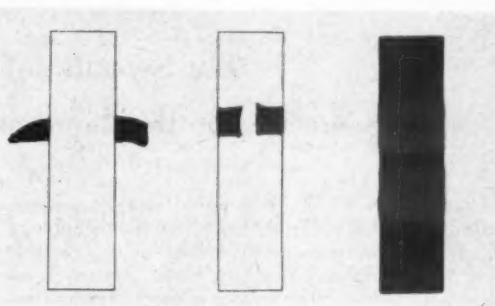

FIG. 2   FIG. 3   FIG. 4

APPENDIX III

Application of Tests to Certain Dyes

(The figure corresponding to the optimum dyeing method for each dye is printed in **bold type**)

Colour Index No.		Dyeing Method						Strike			Levelling			Migration		
		I	II	III	IV	V	VI	20°c.	50°c.	60°c.	20°c.	50°c.	60°c.	20°c.	50°c.	80°c.
	COTTON (40s/2 BLEACHED AMERICAN)															
—	Caledon Yellow 5G (ICI) ...	**5**	5	5	—	—	—	—	—	4–5	—	—	4–5	—	1	4–5
—	Caledon Gold Orange 3G (ICI)...	4	**5**	4–5	—	—	—	—	4–5	—	—	5	—	—	2	3–4
—	Cibanone Orange 6R (Ciba) ...	4–5	**5**	3–4	—	—	—	—	3–4	—	—	4–5	—	—	1	4
—	Durindone Pink FF (ICI)* ...	—	—	—	5	5	**5**	—	3	—	—	4	—	—	3	4–5
1162	Caledon Red BN (ICI) ...	3	4	**5**	—	—	—	3–4	4–5	—	5	—	—	1	4	—
—	Cibanone Red 4B (Ciba) ...	4–5	**5**	4	—	—	—	—	3–4	—	—	5	—	—	2	4
—	Caledon Brilliant Purple 4R (ICI)	**5**	5	4	—	—	—	—	—	2–3	—	—	2–3	—	1	2
1135	Caledon Brilliant Violet R (ICI)	3	4	**5**	—	—	—	4	4	—	5	5	—	1	4	—
—	Caledon Violet XBN (ICI). ...	4–5	**5**	5	—	—	—	—	3–4	—	—	5	—	—	2	3–4
—	Caledon Dark Blue BM (ICI) ...	**5**	3–4	3–4	—	—	—	—	—	4	—	—	4–5	—	1	2
1114	Caledon Blue RC (ICI) ...	**5**	4	4–5	—	—	—	—	—	3–4	—	—	4–5	—	1	2–3
—	Ciba Blue 2RH (Ciba)† ...	—	—	—	4–5	**5**	4–5	—	3	—	—	5	—	—	2	4
1101	Caledon Jade Green XN (ICI) ...	**5**	5	5	—	—	—	—	—	2–3	—	—	3–4	—	1	3–4
—	Caledon Olive Green B (ICI) ...	4–5	**5**	3	—	—	—	—	3	—	—	4	—	—	1	4–5
1150	Caledon Olive R (ICI)	4	**5**	4	—	—	—	—	4	—	—	4–5	—	—	2	4
1151	Caledon Brown R (ICI) ...	4–5	**5**	4–5	—	—	—	—	3–4	—	—	5	—	—	1	2
	MERCERISED COTTON (40s/2 BLEACHED EGYPTIAN)															
—	Caledon Gold Orange 3G (ICI) ...	4–5	4–5	**5**	—	—	—	4	4	—	4	4–5	—	1	1	—
1162	Caledon Red BN (ICI)	3	4	**5**	—	—	—	5	3–4	—	4–5	4–5	—	1	4	—
—	Caledon Brilliant Purple 4R (ICI)	**5**	5	5	—	—	—	—	—	2	—	—	4	—	1	2
1135	Caledon Brilliant Violet R (ICI).	4	4–5	**5**	—	—	—	3	4	—	5	5	—	1	4–5	—
—	Caledon Dark Blue BM (ICI) ...	**5**	4–5	4	—	—	—	—	—	2	—	—	3	—	1	1
1101	Caledon Jade Green XN (ICI) ...	**5**	4–5	4	—	—	—	—	—	3	—	—	3–4	—	1	4
	LINEN (35s BLEACHED LINE YARN)															
—	Caledon Gold Orange 3G (ICI)...	4	**5**	4–5	—	—	—	—	3	—	—	5	—	—	1–2	3
—	Durindone Pink FF (ICI) ...	—	—	—	5	5	**5**	—	3	—	—	4	—	—	1	3
—	Cibanone Red 4B (Ciba)	4–5	4–5	**5**	—	—	—	1	4	—	4–5	4–5	—	2	3	—
1114	Caledon Blue RC (ICI)	**5**	4	4	—	—	—	—	—	3	—	—	4–5	—	1	2
1101	Caledon Jade Green XN (ICI) ...	4–5	**5**	4	—	—	—	—	3	—	—	4	—	—	1	3
	VISCOSE RAYON (150/27 BRIGHT)															
—	Caledon Gold Orange 3G (ICI) ...	4–5	**5**	4	—	—	—	—	4	—	—	5	—	—	2	3–4
—	Cibanone Red 4B (Ciba) ...	**5**	3–4	2	—	—	—	—	—	4	—	—	5	—	1	3
1162	Caledon Red BN (ICI) ...	**5**	5	5	—	—	—	3–4	3	—	4–5	4–5	—	1	2–3	—
1135	Caledon Brilliant Violet R (ICI).	4	**5**	4	—	—	—	—	3	—	—	5	—	—	2–3	5
1114	Caledon Blue RC (ICI)	**5**	5	3	—	—	—	—	—	3	—	—	3	—	1	2–3
1101	Caledon Jade Green XN (ICI) ...	**5**	5	5	—	—	—	—	—	2–3	—	—	3	—	1	3–4

* Vatted at 80°c.   † Vatted at 50°c.

References

[1] *Report of the Committee on the Dyeing Properties of Wool Dyes*, J.S.D.C., **66**, 219 (April 1950).
[2] Clibbens and Geake, *J. Textile Inst.*, **19**, T 77 (1928).

WEST RIDING SECTION

Meeting held at the Midland Hotel, Bradford, on 28th April 1950, Mr. F. SCHOLEFIELD,
President of the Society, in the chair

The Seventh John Mercer Lecture

Some Recent Developments in the Theory of Dyeing

A. B. MEGGY

It is now over a century since John Mercer was making the great contributions to textile technology which are associated with his name, and it is suitable that we should consider how these contributions came to be made. The science of chemistry was in a stage of rapid development and growth in Mercer's time. The discoveries of investigators from Lavoisier onwards had placed the principles of inorganic chemistry on a secure basis, and contributed a large amount of factual knowledge. Organic chemistry was also developing, although the great development, the discovery of synthetic dyes, which was to prove such a powerful stimulus, lay still in the future.

Mercer took the available knowledge of the time, and applied it to the textile industry. His name is principally associated with the process for treating cotton with caustic soda to improve its lustre and its dyeing properties, but he made many contributions to the textile printing industry, and it is in his inventions in this field that his knowledge of chemistry was most notably displayed.

During the past half century the branch of science known as physical chemistry has grown to great proportions, and much progress has been made in applying this knowledge to the textile industry, both to explain existing processes and to develop new ones. It is proposed in this lecture to show how, and with what success, this knowledge has been applied to the study of the dyeing process. The theory of dyeing has made great progress in the last few years, and many of the most important developments are due to the efforts of investigators in this country.

A theory of dyeing must explain the phenomena of the dyeing process in terms of the same physical and chemical ideas as have been found to apply in other fields, and it must not postulate the existence of phenomena peculiar to itself. It must use the common currency of science.

Much progress has been made towards a theory of dyeing which satisfies these conditions. There are two aspects of the dyeing process, as of any other physicochemical process. First, the thermodynamic aspect: this requires the study of the conditions governing the equilibrium of a system when sufficient time has elapsed to allow all change to cease. Secondly, there is the kinetic aspect: this requires the study of the rate at which the system changes towards the equilibrium condition, and of the factors which determine the rate of change. The usual methods of physical chemistry can be applied to both aspects of the problem. The conditions at equilibrium in a reacting system are governed by the free energy change accompanying the reaction; the rate of reaction is governed by the activation energy for the process.

It is best to consider each as a separate problem, and to determine the free energy of dyeing first. It is also convenient at this point to settle a question of nomenclature which otherwise could cause confusion. The free energy change accompanying a chemical reaction is often referred to as the *affinity* of the reaction. Hence, the free energy change accompanying the absorption of a dye by a fibre may be called the affinity of the dye for the fibre. The term "affinity" used in this way has a precise meaning, and the magnitude of the affinity for a particular dye and fibre varies only with temperature, and is independent of pH and the presence of electrolytes. The term "affinity" is also widely used by dyers in a rather imprecise way. Its meaning varies, but in general one dye is said to have a greater affinity than another when more of it is absorbed by the fibre under the usual conditions and time of dyeing. This may involve a confusion between the absorption after a limited period of time, e.g. thirty minutes, and the absorption after sufficient time has elapsed to allow equilibrium to be reached. The dye which has the greater affinity (in the thermodynamic sense) will show the greater absorption at equilibrium, but may show less absorption during the early stages of dyeing, because it is absorbed more slowly. Hereafter the term "affinity" will be used in the thermodynamic sense, to denote the change in free energy when one gram-molecule of a dye is transferred from its standard state in water to its standard state in the fibre, the temperature being defined.

In order to simplify the problem as much as possible, it is best to omit from consideration for the present those dyes in which chemical changes, subsequent to absorption by the fibre, play a part in attaching the dye to the fibre, since it is in practice very difficult to devise experiments which distinguish between absorption by the fibre and subsequent reaction with the fibre. Thus, chrome dyes and other mordant dyes are best considered apart, as the formation of dye–metal–fibre complexes gives rise to complications not present with the acid, direct, and cellulose acetate dyes.

The dyeing process consists in the transfer of the dye from one phase, the dyebath, to another, the fibre. This transfer may be accompanied by the transfer of other material. Most dyes are the salts of sulphonic acids. When the acid anion, the dye molecule proper, migrates from the solution to the

fibre, it must take with it an equivalent number of cations, or displace an equivalent number of anions. Otherwise very large differences of electrical potential would be set up. The small differences of potential which exist between fibres and solutions are due in part to ions not being absorbed in exactly equivalent amounts. As the lack of equivalence is confined to the surface of the fibre, the total difference, calculated on the total amount of ions in the fibre, is too small to be significant when dealing with dyed fibres.

The transfer of inorganic ions which accompanies the dyeing process varies according to the dye and the fibre. A direct dye, when absorbed by cellulose, takes with it sodium ions into the fibre. A dye acid, when absorbed by a protein fibre, takes with it an equivalent number of hydrogen ions into the fibre. The ion of an acid dye, being absorbed by wool in a bath containing sulphuric acid, displaces sulphate ions from the fibre. A dispersed dye is electrically neutral, and its absorption by the fibre does not involve the transfer of inorganic ions.

The absorption of dye may involve a change in the degree of hydration of the fibre, and hence a transfer of water molecules.

To determine the affinity of a dye the following steps are necessary—

(1) Decide by experiment what ions and molecules are involved in the transfer of the dye from the solution to the fibre. This will include the dye ions, and the equivalent number of other ions to maintain electrical neutrality. It should also, in principle, include any water molecules which take part. As water is present in large excess in technical dyeing operations, the change in the activity of water in the fibre and in the dyebath, resulting from the absorption of dye, will be small, and may be neglected. In extreme conditions such as the absorption of dye from a dyebath of small volume and high concentration, and especially if the fibre is capable of taking up large amounts of water of hydration, the transfer of water could involve a significant change in the free energy of the system. Conditions approaching these are found in the steaming of printed textiles.

(2) The second step is to find how the free energy of each of the reacting substances varies with its concentration, both in the water phase and in the fibre phase, and to define standard states for both phases. This problem is simple in principle for the water phase, as the usual equations applicable to solutions of electrolytes can be employed. If $\mu(T)$ is the chemical potential of the substance, and $\mu^\circ(T)$ the chemical potential in the standard state, both at absolute temperature T, and a the activity of the substance in the solution, then—

$$\mu(T) = \mu^\circ(T) + RT \ln a \qquad (i)$$

The activity a of a substance can be directly measured only in a limited number of cases, e.g. when it reacts as part of a reversible electrode system. In such a case the electrode potential varies directly with the chemical potential, that is, with $\ln a$. Such instances are exceptional; in general the activity cannot be measured directly,

but the molarity c (gram-molecules per litre) can be. In dilute solutions—

$$a = c$$

and for non-electrolytes this relation holds for moderately concentrated solutions. For electrolytes, however, appreciable deviations from this ideal behaviour occur even at concentrations of 0.01 M. It is therefore necessary to use a correction factor, the activity coefficient f, such that—

$$a = cf$$

Equation (i) then becomes—

$$\mu(T) = \mu^\circ(T) + RT \ln c + RT \ln f \qquad (ia)$$

The values of f and $\ln f$ are known for most simple inorganic electrolytes. Table I gives the value of f for sodium chloride and sulphate and for hydrochloric and sulphuric acids for a range of concentrations at 25°C. In general, temperature has only a second-order effect on the value of f for these simple electrolytes. The total concentration of ions is the determining factor in mixtures.

TABLE I

Activity Coefficients at 25°C.

Molality*		0·01	0·02	0·05	0·1	0·2	0·5	1·0	2·0
HCl	...	0·905	0·875	0·830	0·796	0·767	0·757	0·809	1·009
H_2SO_4	...	0·545	0·445	0·341	0·266	0·210	0·155	0·131	0·125
NaCl	...	0·904	0·875	0·823	0·778	0·732	0·679	0·656	0·670
Na_2SO_4	...	0·714	0·641	0·53	0·45	0·36	0·27	0·20	—

There are no data on the activity coefficients of dyes of the types used technically, although some measurements have been made on picric acid and methylene blue. Therefore one must use molarities in place of activities in equation (i). This introduces an error of $RT \ln f$ into the expression for the free energy of the dye in aqueous solution. If f were constant over the range of conditions studied, $RT \ln f$ would be included in the affinity of the dye, and it would not prevent constant values for the affinity from being obtained. In fact, however, it is very probable that f for the dye varies considerably, both with temperature and with the ionic concentration, and is greater than unity in most cases. For the inorganic electrolytes, on the other hand, f is less than unity, except in very concentrated solutions of some electrolytes.

Although the determination of the absolute values of the activity coefficients of dyes would be a difficult and tedious task, it is an easy matter to follow the effect of a change in the electrolyte concentration on the activity coefficient, from the change in the solubility of the dye. The method of doing this is described in the standard textbooks[1]. The method enables kf to be calculated, k being an unknown constant. Fig. 1 shows log kf for Orange II plotted as a function of the logarithm of the ionic concentration in equivalents per litre. One curve shows the behaviour of the sodium salt in solutions of sodium sulphate and sodium chloride; the other, the behaviour of the free acid in the presence of hydrochloric acid. It will be seen that log kf increases with increasing ionic concentration, and that the increase is particularly rapid when the concentration of the electrolyte is greater than 0.1 N. Although the curves are similar in appearance, the different ions exercise specific effects;

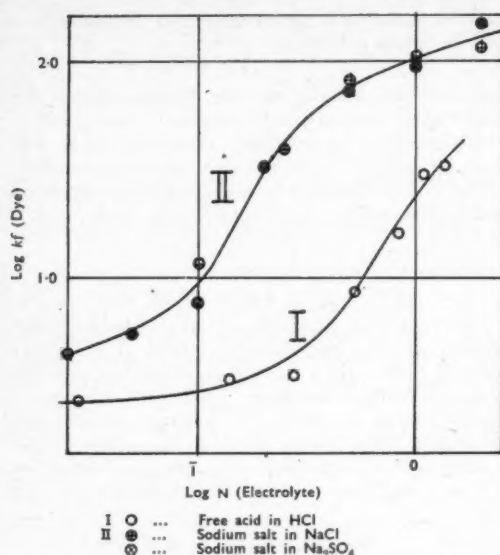* Molality = g.mol. per 1000 g. solvent
  Molarity = g.mol. per litre

FIG. 1—Effect of Added Electrolyte Concentration on the Activity Coefficient of Orange II at 25°c.

Legend:
I   O   ...   Free acid in HCl
II   ⊕   ...   Sodium salt in NaCl
  ⊗   ...   Sodium salt in Na₂SO₄

Y-axis: Log kf (Dye); X-axis: Log N (Electrolyte)

f is not a function of the ionic concentration alone. It is obvious that the great increase in f with increasing electrolyte concentration at the temperature of these measurements, which was 25°C., is too large to be neglected. On the other hand, it appears, from observations on the salting out of Orange II at various temperatures, that the effect of electrolytes on the activity coefficient is much less at high temperatures. Orange II is readily soluble in N. sodium chloride at 60° C. It also seems probable that the effect is less with poly-sulphonic acid dyes.

The relation between free energy and concentration in the fibre phase has next to be determined. This is the most difficult problem to be solved in the thermodynamic treatment. Generally speaking, each type of fibre represents a separate problem: there is no general solution.

The first successful treatment was that proposed by Rideal and Gilbert[2]. They were considering the combination of insoluble fibrous proteins, such as wool and silk, with mineral acids such as hydrochloric acid. They suggested that the ions might be regarded as absorbed on a limited number of sites in the fibre, corresponding to the carboxyl and amino groups present. To this system they applied an expression used by Langmuir for the free energy of neutral atoms adsorbed on a metal crystal. The original paper should be consulted for a detailed treatment. The result was that the free energy of a proton on the wool fibre was given by the expression—

$$\mu_{H^+} = \mu_{H^+}{}^\circ + RT \ln \frac{\theta}{1-\theta} + V\boldsymbol{F} \qquad \text{(ii}a\text{)}$$

and that of a chloride ion by—

$$\mu_{Cl^-} = \mu_{Cl^-}{}^\circ + RT \ln \frac{\theta}{1-\theta} - V\boldsymbol{F} \qquad \text{(ii}b\text{)}$$

where θ is that fraction of the total number of sites available for occupation which are actually occupied, μ° the chemical potential when half the

sites are occupied, V the difference in potential between the fibre and the solution, and $\boldsymbol{F}$ is Faraday's constant.

Combining equations (i) and (ii), and putting—

$$\Delta\mu_{H^+} = \mu_{H^+}{}^\circ \text{(fibre)} - \mu_{H^+}{}^\circ \text{(soln.)}$$

$$\Delta\mu_{Cl^-} = \mu_{Cl^-}{}^\circ \text{(fibre)} - \mu_{Cl^-}{}^\circ \text{(soln.)}$$

we obtain—

$$RT \ln \frac{\theta}{1-\theta} - RT \ln \{H^+\} + \Delta\mu_{H^+} + V\boldsymbol{F} = 0 \qquad \text{(iii}a\text{)}$$

$$RT \ln \frac{\theta}{1-\theta} - RT \ln \{Cl^-\} + \Delta\mu_{Cl^-} - V\boldsymbol{F} = 0 \qquad \text{(iii}b\text{)}$$

where the braces {} represent molar activities in the external solution. Hence, by addition—

$$2RT\ln \frac{\theta}{1-\theta} - RT\ln \{H^+\} - RT\ln\{Cl^-\} + \Delta\mu_{H^+} + \Delta\mu_{Cl^-} = 0 \qquad \text{(iv)}$$

and by subtraction—

$$RT\ln \{Cl^-\} - RT\ln\{H^+\} + \Delta\mu_{H^+} - \Delta\mu_{Cl^-} - 2V\boldsymbol{F} = 0 \qquad \text{(v)}$$

The quantities θ, $\{H^+\}$, and $\{Cl^-\}$ in equation (iv) can be calculated from the data on the absorption of hydrochloric acid by wool in the presence of sodium chloride. The values of $(\Delta\mu_{H^+} + \Delta\mu_{Cl^-})$ thus obtained, from experiments in which θ varied from 0·05 to 0·95, and the chloride ion concentration from 0·005 to 1·0 N., were reasonably constant, the mean value being 5750 g.cal. at 0°C. (Table II).

TABLE II

Affinity of Hydrochloric Acid for Wool at 0°C.

Ionic strength	...	1·0	0·5	0·2	0·1
$-\Delta\mu_{HCl}$, g. cal.	...	5533	5726	5838	5747
Ionic strength	...	0·04	0·02	0·01	0·005
$-\Delta\mu_{HCl}$, g. cal.	...	5747	5774	5843	5780
	Mean value	...	5750 g. cal.		

If wool is being treated with pure hydrochloric acid solutions, containing no excess of chloride ions, $[H^+] = [Cl^-]$. Furthermore, at the point of half titration, $\theta = 0·5$, so that $\ln \theta/(1-\theta)$ is zero. Consequently, at the point of half titration—

$$\Delta\mu_{H^+} + \Delta\mu_{Cl^-} = 2RT \ln \{H^+\} = -2·303 \times 2RT(\text{pH})^* \quad \text{(iv}a\text{)}$$

where (pH) is the pH of the external solution when the wool is half-titrated with acid. Table III gives the affinities of several acids calculated from equation (iva) and the data of Steinhardt, Fuggitt, and Harris[3]. The combining capacity of wool is assumed to be 0·82 milliequivalent per gram, so that the pH in (iva) is that at which there is 0·41 equivalent of acid bound.

The application of equation (iv) always gives $(\Delta\mu_{H^+} + \Delta\mu_{A^-})$, the sum of the affinities of the hydrogen ion and anion. Equation (v) contains the difference of the affinities, and it is possible, in principle, to calculate $(\Delta\mu_{H^+} - \Delta\mu_{A^-})$, the difference in the affinities of the hydrogen ion and the anion. From this it would be possible to calculate the affinities of the individual ions. But the use of equation (v) requires a knowledge of the value of V, the difference in potential between the fibre and the solution. This quantity cannot be measured directly, at any rate not in a simple manner, and this is a serious difficulty in using equation (v).

* Assuming activity = concentration; this is a reasonable approximation for the conditions under which this equation is applied

TABLE III
Affinity of Various Acids for Wool calculated from the pH of Half Saturation

Acid	Mol. Wt.	(pH)	$-(\Delta\mu_{H^+} + \Delta\mu_{A^-})$	$-\Delta\mu_{A^-}$ $(\Delta\mu_{Cl^-}=0)$
AT 0°C.				
Hydrochloric	36·5	2·32	5760	0
Ethylsulphuric	126	2·33	5800	40
Hydrobromic	81	2·47	6150	390
Nitric	63	2·58	6410	650
*iso*Amylsulphonic	152	2·58	6410	650
Benzenesulphonic	158	2·63	6550	790
p-Toluenesulphonic	172	2·66	6600	840
o-Phenolsulphonic	174	2·66	6600	840
o-Xylene-*p*-sulphonic	186	2·71	6750	990
Metaphosphoric	80	2·72	6760	1000
Trichloroacetic	·163·5	2·73	6800	1040
o-Nitrobenzenesulphonic	203	2·86	7120	1360
Pyrophosphoric	178	2·94	7300	1540
5-Nitro-2-chlorobenzene-sulphonic	237·5	3·07	7640	1880
2:5-Dichlorobenzenesulphonic	227	3·13	7780	2020
2:4-Dinitrobenzenesulphonic	248	3·17	7880	2120
β-Naphthalenesulphonic	208	3·24	8050	2290
2:4:6-Trinitroresorcinol	245	3·64	9050	3290
Picric	229	3·86	9600	3840
Flavianic	314	4·24	10,530	4770
AT 25°C.				
Hydrochloric	36·5	2·16	5770	0
β-Naphthalenesulphonic	208	3·03	8250	2480
Octylsulphuric	210	3·47	9450	3680
Sulphosalicylic	218	3·34	9100	3330
Picric	229	3·52	9550	3780
Dodecylsulphuric	266	4·02	10,920	5150
Flavianic	314	4·07	11,050	5280
Dodecylsulphonic	250	4·08	11,100	5330
AT 50°C.				
Hydrochloric	36·5	2·17	6400	0
β-Naphthalenesulphonic	208	2·95	8700	2300
p-Diphenylsulphonic	234	3·16	9320	2920
pp'-Hydroxyazobenzene-sulphonic	278	3·24	9550	3150
2-Anthraquinonesulphonic	288	3·40	10,020	3620
Diphenylbenzenesulphonic	310	3·70	10,900	4500
*iso*Propylnaphthalene-sulphonic	250	3·74	11,200	4800
Dodecylsulphonic	250	3·96	11,700	5300

But, although V is difficult to measure, it is relatively easy to decide when it has the value zero, i.e. when there is no potential difference between the fibre and the solution. This can be done by observing the movement of wool particles in an electric field[4], or from the streaming potential set up when a solution flows past a plug of wool[5].

From (v), when $V = 0$—

$$\Delta\mu_{H^+} - \Delta\mu_{Cl^-} = RT \ln \{H^+\} - RT \ln \{Cl^-\} \qquad (va)$$

From the results of Neale on the electrokinetic potential, $V = 0$ at pH 3·3 when the chloride ion concentration was 0·001 N. Substituting these values in (va)—

$$\Delta\mu_{Cl^-} - \Delta\mu_{H^+} = 2\cdot303\,RT\,(\log\{Cl^-\} - \log\{H^+\})$$
$$= 396\ \text{g. cal.}$$

$$\Delta\mu_{H^+} + \Delta\mu_{Cl^-} = -5800\ \text{g. cal. at } 25°\text{c.}$$

Hence

$$\Delta\mu_{H^+} = -3100\ \text{g. cal.}$$

and

$$\Delta\mu_{Cl^-} = -2700\ \text{g. cal.}$$

These results are inconsistent with the known properties of wool, and the data on the dissociation constant of the carboxyl group in amino acids and other acids. Wool combines readily with hydrochloric acid, even at pH 5, if excess chloride ions are present. On the other hand, it shows no tendency to absorb sodium chloride, even in strong

solutions. One has the impression that the combination of mineral acids with wool is principally due to the affinity of the hydrogen ions, and this is in agreement with the known affinity of the hydrogen ion for the carboxyl group. Organic acids usually have dissociation constants of the order of 10^{-4}, which corresponds to an affinity of about 6000 calories ($\Delta G = RT \ln K$).

There are several possible explanations for these results. The two most probable are as follows. It should be borne in mind that the data for applying equation (v) are derived from experiments which are concerned with the surface of the wool fibre, whereas those for applying equation (iv) are concerned with the whole bulk. If the composition of the surface area differed from that of the bulk, this would give rise to inconsistencies. The ratio of amino to carboxyl groups in wool is very nearly 1 : 1, and in developing equation (v) it has been assumed that the ratio in the surface layer is the same. This is not necessarily the case: chemical reaction at the exposed surface could alter the ratio, and mechanical rupture would tend to take place along planes of weakness, which might have a different composition from that of the bulk. An alternative possibility is that part of the potential drop between the fibre and the solution takes place within the fibre itself, so that, although the external solution is at the same potential as the surface of the fibre, the interior of the fibre is at a different potential. It is difficult to see why a potential gradient should exist within the fibre when there is none between the surface of the fibre and the external solution. The first explanation therefore seems preferable.

Since the attempt to use equation (v) to determine the separate values of $\Delta\mu_{H^+}$ and $\Delta\mu_{Cl^-}$ experimentally fails, some arbitrary division of the total affinity between the anion and the cation must be made. The simplest assumption is to assign the whole of the affinity of hydrochloric acid to the hydrogen ion at all temperatures, so that $\Delta\mu_{Cl^-} = 0$. In Table III, by subtracting the value of $\Delta\mu_{H^+}$ from the total affinity, the value of $\Delta\mu$ for the anion is obtained, as shown in the last column.

The above assumption is quite consistent with the known dissociation constants of aspartic and glutamic acids, whose free carboxyl groups are responsible for the combination of hydrogen ions with wool. For aspartic acid K is $10^{-3\cdot87}$, and for glutamic acid it is $10^{-4\cdot21}$, at 25°c. These correspond to affinities of 5260 and 5720 g.cal. respectively, while the affinity of hydrochloric acid for wool at this temperature is 5800 g.cal.

Equation (iv) can be used to determine the affinity of any univalent anion for wool, on the assumption that $\Delta\mu_{Cl^-} = 0$. It is also possible to measure the affinity of a univalent anion against chloride ion directly. If two univalent anions are present on the fibre, equation (iiib) applies to each ion separately—

$$RT \ln \frac{\theta_{Cl^-}}{1 - \theta_{A^-} - \theta_{Cl^-}} - RT \ln \{Cl^-\} + \Delta\mu_{Cl^-} - VF = 0$$

$$RT \ln \frac{\theta_{A^-}}{1 - \theta_{A^-} - \theta_{Cl^-}} - RT \ln \{A^-\} + \Delta\mu_{A^-} - VF = 0$$

A3

By subtraction—

$$RT \ln \frac{\theta_{A^-}}{\theta_{Cl^-}} - RT \ln \frac{\{A^-\}}{\{Cl^-\}} + \Delta\mu_{A^-} - \Delta\mu_{Cl^-} = 0 \quad \text{(vi)}$$

If θ_{A^-} and θ_{Cl^-} are the fractions of available sites occupied by chloride ion and other anion respectively, the fraction of sites not occupied is $1 - (\theta_{A^-} + \theta_{Cl^-})$. All the quantities in equation (vi) can be determined experimentally. If A^- is a coloured ion, it can be measured colorimetrically, directly in the solution, and after stripping from the fibre. The chloride ion concentration in the solution can be measured directly, but its determination on the fibre is not quite so simple. However, if in the case of wool the experiments are carried out at pH 2, i.e. in 0·01 N. hydrochloric acid, substantially all the sites in the fibre are occupied by chloride ions or other anions. Under these circumstances θ_{Cl^-} is approximately equal to $(1 - \theta_{A^-})$, and equation (vi) may be written—

$$RT \ln \frac{\theta_{A^-}}{1 - \theta_{A^-}} - RT \ln \frac{\{A^-\}}{\{Cl^-\}} + \Delta\mu_{A^-} - \Delta\mu_{Cl^-} = 0$$
$$\text{(via)}$$

θ_{A^-}, $\{A^-\}$, and $\{Cl^-\}$ can all be obtained from equilibrium measurements, so that $(\Delta\mu_{A^-} - \Delta\mu_{Cl^-})$ can be calculated. For the dye ion it must be assumed that the activity is the same as the concentration.

Table IV gives the affinities of some univalent dye anions on wool, obtained by using equations (iv) and (via), taken from the paper by Lemin and Vickerstaff[6]. Table V gives the affinity of Metanil Yellow YK for various values of θ; the constancy

TABLE IV
Affinity of Various Dye Anions for Wool at 60°C.

Code	Dye	Mean Affinity (g. cal.)	Individual Affinity	Method	Theoretical Affinity
A	Naphthalene Orange G ...	−4200	−3800	Free acid	−9200
			−4600	Desorption	(Fig. 6)
B	Solway Ultra Blue B	−7000	−7100	Desorption	—
			−6900	Competition with A	
C	Metanil Yellow YK	−5200	−5000	Free acid	—
			−5300	Competition with B	
D	Solway Purple R ...	−6600	−6500	Competition with A	—
			−6700	Competition with C	
E	Solway Blue R ...	−6600	−6200	Free acid	−9,700
			−6600	Competition with A	(Fig. 9)
			−6900	Competition with C	
F	Coomassie Red G...	−6500	−6500	Free acid	−10,400 (Fig. 7)

TABLE V
Affinity of Metanil Yellow YK at Various Degrees of Absorption at 60°C.

Concentration of Dyebath ($\times 10^{-3}$ M.)	pH	θ	Affinity (g. cal.)
0·0508	5·77	0·041	−11,100
0·140	5·83	0·074	−11,400
0·236	5·77	0·103	−11,400
0·337	5·58	0·142	−11,400
0·405	5·48	0·185	−11,500
0·441	5·27	0·216	−11,400
0·554	5·30	0·266	−11,700
0·555	4·92	0·311	−11,400
0·634	4·63	0·440	−11,600
1·24	3·98	0·615	−11,100

Mean affinity $(\Delta\mu_{H^+} + \Delta\mu_{A^-}) = -11,400 \pm 190$ g. cal.

$\overline{5}$

$\overline{4}$

Log [Dye Anion]

$\overline{2}$ $\overline{1}$

Log $\{SO_4{}^{2-}\}$

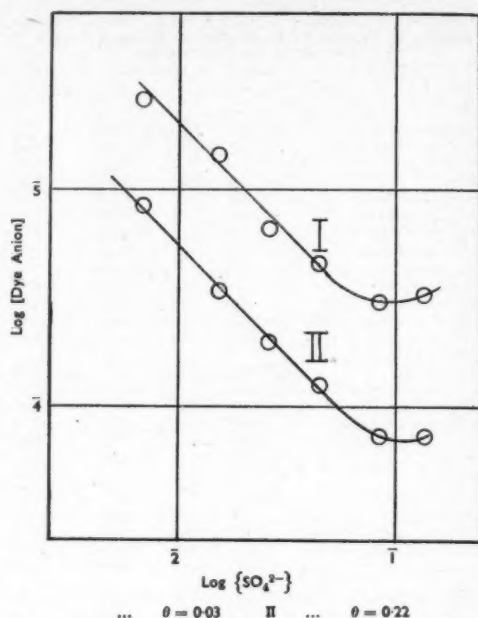... $\theta = 0·03$ II   ... $\theta = 0·22$

FIG. 2— Desorption of Azogeranine by Sodium Sulphate at 60°C.

of the values is evidence of the validity of equation (iv).

In Fig. 2 and 3 data are given graphically for the desorption of mono- and di-sulphonic acid dyes by chloride and sulphate at 60°C. If the composition of the dyed fibre is kept constant, the first term in equation (via) is constant, and the equation simplifies to—
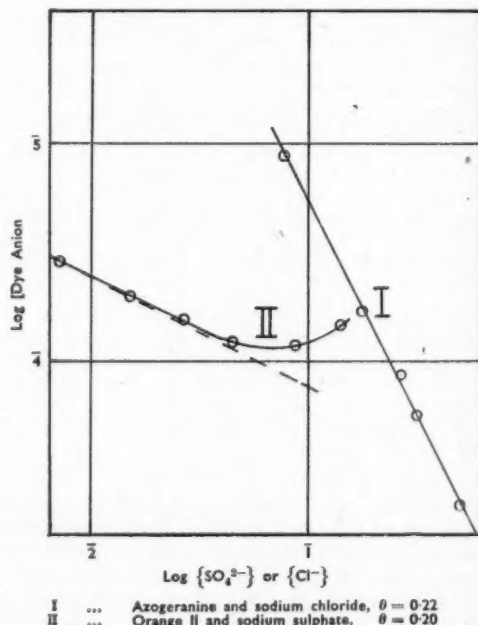
$$RT \ln \{A^-\} - RT \ln \{Cl^-\} = \text{constant}$$

$\overline{5}$

$\overline{4}$

Log [Dye Anion]

$\overline{2}$ $\overline{1}$

Log $\{SO_4{}^{2-}\}$ or $\{Cl^-\}$

I   ...   Azogeranine and sodium chloride, $\theta = 0·22$
II   ...   Orange II and sodium sulphate, $\theta = 0·20$

FIG. 3— Desorption of Azogeranine and Orange II at 60°C.

Consequently, the plot of log $\{A^-\}$ against log $\{Cl^-\}$ should be a straight line, with a slope of $+1$. For the desorption of a bivalent dye by sulphate, the slope should also be $+1$, since one dye ion is replaced by one sulphate ion. If a bivalent dye ion is desorbed by chloride the slope should be 2, since two chloride ions replace each dye ion; if a univalent dye ion is desorbed by sulphate the slope should be 0·5. In Fig. 2 and 3 the logarithm of the *concentration* of the dye ion is plotted against the logarithm of the *activity* of the sulphate or chloride ion, as the activity coefficients of the dye ions are not known. Since—

$$\log a = \log c + \log f$$

the above relations will still hold if f is constant over the range of conditions considered, or if the variation of f from unity is small. It will be seen that in Fig. 2, the desorption of Azogeranine by sodium sulphate, the agreement with the theory is good within the limits of experimental error, up to a sulphate concentration of 0·05 M.; at higher concentrations the graph is not linear. It seems very probable that the increase in the activity coefficient of the dye is responsible for this. It is interesting to observe that this increase may go so far as to neutralise, or even reverse, the usual stripping action of sodium sulphate.

The graphs in Fig. 3 show the desorption of Azogeranine by sodium chloride, and of Orange II by sodium sulphate. The Azogeranine graph has the theoretical slope of 2 to the highest concentration of sodium chloride used, 0·5 M. It seems that the univalent chloride ion has little effect on the activity of the bivalent dye ion. On the other hand, the Orange II graph has not the theoretical slope of 0·5 at any point; even in 0·01 M. sodium sulphate it is perceptibly less; the broken line shows the theoretical slope. The activity coefficient is increasing all the time, and already at 0·05 M. the stripping effect is neutralised; an increase in the sulphate concentration is balanced by an increase in the activity coefficient of the dye, and beyond 0·1 M. an increase in sulphate causes less dye to be desorbed.

Reference to Fig. 1 shows that the increase in log f is very rapid with increase in the electrolyte concentration. The values in Fig. 1 were obtained at 25°c., owing to experimental difficulties in working at higher temperatures, whereas those in Fig. 3 were obtained at 60°c. As the activity coefficient varies considerably with the temperature a direct application of the data in Fig. 1 is not possible. However, it seems that the following conclusions may be drawn— (1) The activity coefficients of sulphonic acid dyes increase with increasing electrolyte concentration, particularly in solutions stronger than 0·05 M. (2) Bivalent electrolytes have a greater effect than univalent. (3) Monosulphonic acid dyes are more susceptible than disulphonic. (4) The effects are less at high temperatures.

The graphs similar to those in Fig. 2 and 3 have been drawn for a large number of dyes by Gilbert[7] from the data of Speakman and Clegg[8].

The measurement of affinities has been extended to direct dyes by Marshall and Peters[9]. Here,

again, the principal difficulty was to determine the function for the concentration–free energy relationship for the dye on the fibre. The calculations were based on the assumption that there was a definite volume of the fibre available to the dye, in which the dye behaved as though in solution. This volume varied for the different forms of cellulose, its value in litres per kilogram being 0·22 for cotton, 0·45 for viscose rayon and Cellophane, and 0·60 for cuprammonium rayon. The original paper should be consulted for the method of calculation, which is applicable to other fibres. No account was taken in these calculations of the activity coefficient of the dye, but since all the dyes were di- or tetra-sulphonic acids, and the electrolyte was sodium chloride, while the temperatures ranged from 60° to 90°c., it is probable that this omission, which was unavoidable owing to lack of the necessary data, did not affect the validity of the results to any appreciable extent.

It will be seen that, although the affinity of the direct dyes for cotton (Table VI) is of the same order as that of the acid dyes for wool, their structure is more complex. The affinity of a direct dye, used as an acid dye on wool, would be far greater, but at present no comparative measurements are available.

<div align="center">

TABLE VI

Affinity of Direct Dyes on Cellulose

(g. cal.)

</div>

Dye	Colour Index No.	Temp. (°c.)	Cotton	Viscose Rayon	Cuprammonium Rayon
Chrysophenine G ...	365	90	−3000	−3100	−2800
		60	−3900	−3900	−3800
Chlorazol Sky Blue FF...	518	90	—	−6300	−6000
		60	—	−7700	−7200
Chlorazol Violet N ...	394	90	—	−4300	−4300
		60	—	−4600	−4900

The affinity defines the behaviour of the dye in the dyebath at equilibrium, at the temperature at which it is measured. It varies with the temperature, and from the temperature coefficient it is possible to calculate the heat of dyeing and the entropy of dyeing. This calculation has been made for the dye Orange 2G by Gilbert. There was found a large entropy of dyeing, amounting to about 19 g.cal./°c.; this indicates that the dye is subject to considerable restriction within the fibre, as compared with a sulphate ion[7].

The question naturally arises—what determines the affinity? How is it related to the chemical structure of the dye, and can it be varied in a predictable way by varying the structure? This is merely a variation of an old question—what is the nature of the forces holding the dye to the fibre?

Dyes show the most varied range of chemical structures, even dyes for a particular fibre. They contain many groups which have considerable affinity for water, such as hydroxyl, amino, azo, and carbonyl groups. These groups are known to have considerable powers of co-ordination, and it might be thought that they are responsible for the forces holding the dye to the fibre. But a study of the structure of some typical dyes shows that the co-ordinating power of these groups is already largely satisfied within the dye molecule by chelation.

Fig. 4 shows the structure of 1:5-dihydroxy-4:8-diaminoanthraquinone, and Fig. 5 that of benzene-azo-β-naphthol. Although (4) has two hydroxyl, two amino, and two carbonyl groups, it is insoluble in water, acids, and alkalis, and is chemically much more stable than, for instance, p-aminophenol. It can be used as a dispersed dye for cellulose acetate and nylon. To make it soluble, one or two sulpho groups are introduced. It then becomes an acid dye for wool, with a rather low affinity. The
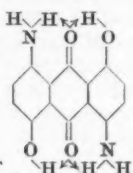
FIG. 4— Chelation in 1:5-Dihydroxy-4:8-diaminoanthraquinone
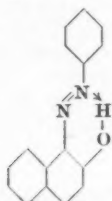
FIG. 5— Chelation in Benzeneazo-β-naphthol

hydroxyl and amino groups are locked up in a strongly chelated structure, and it does not appear that there are any considerable residual valency forces available to form hydrogen bonds with the fibre. Undoubtedly, however, the affinity is due in some way to the organic part of the molecule. The disulphonic acids obtained by introducing two sulpho groups into (4) or (5) readily displace sulphate ions from wool.

Let us consider the affinities of some of the sulphonic acids given in Table III (p. 513). Benzene-sulphonic acid has a slight affinity for wool, 6550 g. cal., a little greater than hydrochloric acid. Two nitro groups, the most powerful co-ordinating agent, raise this to 7880 g.cal. Naphthalenesulphonic acid has an affinity of 8050 g.cal., which is greater than that of the dinitro compound. It follows from this that the addition of the second aromatic ring has a greater influence on the affinity than the addition of two nitro groups.

The affinities of several alkylsulphuric acids are given in the table. They are— for ethylsulphuric 5800, for octylsulphuric 9450, and for dodecyl-sulphuric 10,920 g.cal.

It will be seen that the affinity increases progressively by about 400 g. cal. per carbon atom for the unbranched chains. With these compounds the formation of hydrogen bonds between the compound and the fibre can be excluded, and the van der Waals forces are at a minimum.

It appears that the principal factor determining the affinity of sulphonic acids for wool is the size of the hydrocarbon skeleton. It should be noted that the above effect of alkyl chains on the affinity holds good when the alkyl chain is attached to a

aromatic ring. The introduction of alkyl chains into a dye molecule does not greatly affect the colour of the dye, but it does increase the affinity for wool. Thus, the introduction of a chain of eight or twelve carbon atoms into a simple acid dye will turn it into a milling dye of the same hue. This useful discovery was made empirically, and has been exploited for some time.

The increase of affinity with chain length shown by the alkylsulphuric acids reminds one irresistibly of the increase of surface activity with chain length shown by these compounds, and leads one to seek an explanation of both phenomena in the same cause. It was suggested by Hartley[10] that the surface activity of paraffin chain salts was due to the attraction of water molecules for each other, and this explanation is widely accepted to-day. The distinction between dyes and other sulphonated hydrocarbons is an artificial one, based on colour, which has no direct connection with the power of being absorbed by fibres. When a sulphonated hydrocarbon is dissolved in water, an interface is formed between each organic molecule and the water molecules; this is substantially a water–hydrocarbon interface. The chelated groups present in most dyes, of which examples have been given, probably also behave as hydrocarbon regions, in that they do not react with water molecules by solvation. The creation of this water–hydrocarbon interface involves the separation of water molecules from each other, and hence the expenditure of energy in breaking hydrogen bonds and overcoming van der Waals forces. This energy is supplied by the solvation of the sulpho or other solubilising groups. If the dye molecule within the fibre is in such an environment that the hydrocarbon residue is in a non-aqueous medium, while the solubilising groups remain solvated, the free energy of the system will decrease on absorption by an amount corresponding to the disappearance of the water–hydrocarbon interface.

A rough calculation can be made of the energy available from this effect. The total surface involved is the surface of a single molecule, counting both sides, multiplied by the number of molecules in a gram-molecule ($6 \cdot 0 \times 10^{23}$). The area of a single molecule can be estimated by drawing it to scale, using the known values for bond lengths, and measuring the area. Four such drawings are shown in Fig. 6–9, with the areas found. The energy of a water–hydrocarbon interface, from surface tension measurements, is about 30 ergs per sq. cm. If A sq. A. is the total area of the molecule from the scale drawing, the total interface is $2A \times 6 \cdot 0 \times 10^7$ sq. cm., since 1 sq. A $= 10^{-16}$ sq. cm. The total energy associated with the interface is—

$$\frac{2A \times 6 \cdot 0 \times 10^7 \times 30}{4 \cdot 18 \times 10^7} = 86A \text{ g.cal./g.mol.}$$

In the last column of Table IV (p. 514) the calculated affinities of some dye anions are given, whose basic hydrocarbon structures are probably similar to those drawn to scale in Fig. 6–9. It will be seen that the affinities of these dyes are considerably less than the calculated values. There are several reasons for this discrepancy— (1) The transfer of the sulpho group from water to the

Area   ...   106 sq. A.
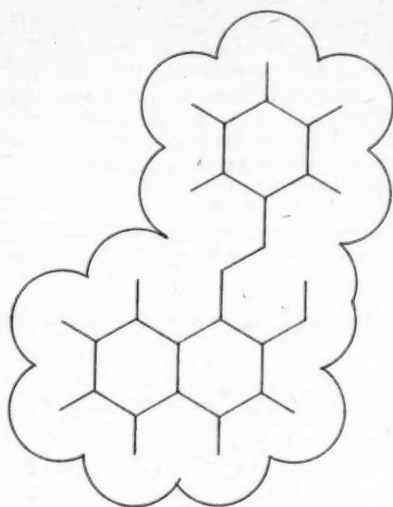
FIG. 6— Scale Drawing of Benzeneazo-β-naphthol

Area   ...   121 sq. A.
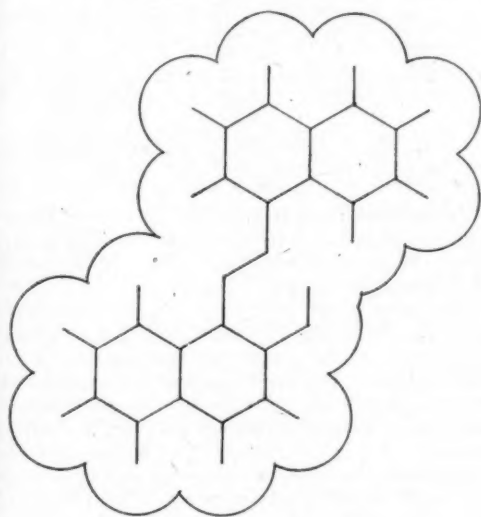
FIG. 7— Scale Drawing of Naphthaleneazo-β-naphthol

Area   ...   91 sq. A.

FIG. 8— Scale Drawing of
1:5-Dihydroxy-4:8-diaminoanthraquinone

Area   ...   113 sq. A.

FIG. 9— Scale Drawing of 1-Phenylamino-4-hydroxyanthraquinone

based on this figure. If a smaller value were used it would have an appreciable effect on the measured area, and on the calculated affinity. There is a good deal of uncertainty as to what the correct value should be.

The calculated affinities should be taken as maximum values; the calculation shows that the disappearance of the water–hydrocarbon interface would account for the affinity of dyes for wool without assuming any forces acting between the dye and the fibre. The calculation can be extended to the paraffin-chain salts, if it is assumed that they can be treated as rods with a cross-section of 18·5 sq. A. and a length of 1·27 A. per carbon atom. The affinity should then increase by about 830 g.cal. per carbon atom; the values given in Table III indicate about 400 g.cal. per carbon atom (p. 516).

These calculations show that the affinity of acid and milling dyes on wool could be due to the disappearance of the water–hydrocarbon interface when the dye is absorbed by the fibre. It does not necessarily follow that this is the only effect involved, but it seems certain that the effect of alkyl groups on the affinity of dyes for wool is due to it.

fibre may involve an increase in the free energy of the system. (2) The value used for the interfacial energy, 30 ergs per sq. cm., is probably too high. The dye molecule is in the form of a thin sheet only one atom thick; consequently the water molecules on each side of it are separated by a distance of about 6 A. At this distance the water molecules probably still exert an appreciable attraction on each other, so that the energy per unit area of interface is less than it would be if they were at a great distance from each other. The value of 30 ergs corresponds to separation to an infinite distance. (3) The measured area may be too large. It was assumed that the nearest distance of approach of two hydrogen atoms not in combination was 3 A. The perimeters of the molecules are

Thus, an important source of the affinity of dyes for fibres is the attraction of water molecules for each other. As this attraction is exceptionally high in the case of water, being equalled by few other substances, there are theoretical reasons for believing that dyeing could not be carried out successfully from any other solvent, even though the dye were soluble in it.

If the dye within the fibre is still wholly or mainly in an aqueous environment, for instance in water within the pores of the fibre, absorption by the fibre does not involve the disappearance of the water–hydrocarbon interface. This is probably the case with some fibres, e.g. cellulose. Here forces between the dye and the fibre probably play a part, as shown by the orientation of the dye with respect to the fibre, and also by the marked way in which the affinity of direct dyes is affected by small changes in structure. It was pointed out earlier (p. 515) that, from Tables IV and VI, the affinity of a direct dye on wool should be greater than that of the same dye on cellulose. On the other hand, a fibre with very slight water absorption, such as nylon, probably absorbs the dye into a non-aqueous environment, and disappearance of the water–hydrocarbon interface is responsible for a large part of the affinity.

The second aspect of the dyeing process is the kinetic aspect, the rate at which dye is absorbed by the fibre. There are a number of observations on the kinetics of dyeing which can be made in any dyehouse. Firstly, the rate of dyeing increases rapidly with temperature. Secondly, those dyes with the best fastness properties dye slowly. This is particularly noticeable among wool dyes: milling dyes dye slower than acid dyes under comparable conditions. Thirdly, the rate of dyeing depends on the physical condition of the fibre. The different forms of cellulose— cotton, mercerised cotton, viscose rayon, and cuprammonium rayon— dye at a rate increasing in the order given. Different batches of viscose may dye at different rates, though if sufficient time is allowed for equilibrium to be attained, the final shades will usually match.

It follows that the rate at which the dye diffuses in the dye liquor can have very little to do with the rate of dyeing; generally it is not the rate at which dye is brought to the surface of the fibre which controls the rate of absorption. If the agitation of the dye liquor is sufficiently vigorous there will always be dye available at the fibre surface.

If cross-sections of the fibre are examined under the microscope as dyeing proceeds, it is found that in the initial stages of dyeing only the outer ring of the cross-section, corresponding to the surface of the fibre, is dyed. As dyeing proceeds, the dye penetrates towards the centre of the fibre, until a uniform dyeing is obtained. This is the picture found, whatever dye and fibre are examined. This relatively slow passage of the dye through the fibre is the process which controls the rate of dyeing.

The uptake of dye follows the law required for a diffusion process. It was shown by Speakman and Smith[11], using acid dyes on wool, that if the amount of dye absorbed was plotted against the square root of the time, the experimental points fell on a straight line until absorption was almost complete. A typical curve is shown in Fig. 10. The slope of the straight portion varied with temperature. More recent experiments, in which the concentration of the dyebath was kept constant during the dyeing, have confirmed the deductions from the earlier work.
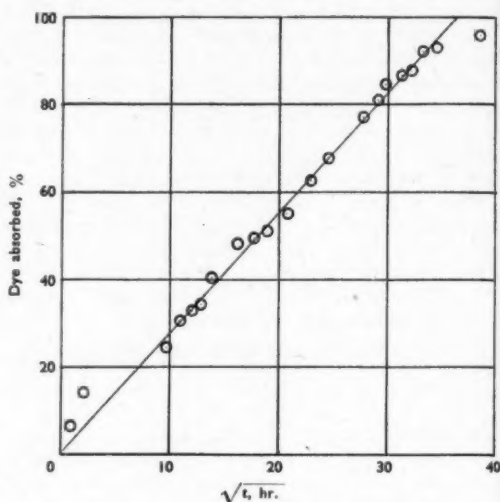

FIG. 10— Rate of Dyeing of Human Hair by Acid Orange 2G at 22°C.

The $\sqrt{t}$ relationship would apply to a substance diffusing from a solution of constant composition into a plate of infinite thickness. In the early experiments these conditions were approximately fulfilled during the first stages of absorption, since the composition of the dyebath had not been altered appreciably by the loss of the small amount of dye absorbed on to the fibre, and the dye on the fibre was in a layer thin in proportion to the radius of the fibre. The gradual exhaustion of the dyebath would tend to slow down diffusion, but this was compensated to some extent by the decrease of the area of the advancing front of dye as it approached the centre of the fibre. These two effects rather tended to balance out, and the $\sqrt{t}$ relationship held over a greater range of the experimental data than would be expected.

A large amount of work has been done on the dyeing of cellulose with direct dyes, particularly the dyeing of viscose rayon and Cellophane. The latter is particularly suitable as a substrate for dyeing experiments, as the surface area can be easily measured. Many experimental results have been published. The general picture which emerges is as follows— The surface of the fibre reaches equilibrium with the dye in the dyebath within a few seconds of the beginning of dyeing. The concentration of dye in this surface layer is the concentration which would be established throughout the fibre if the dyebath were of infinite volume and of the initial concentration. This surface concentration is therefore a function of the affinity of the dye for the fibre. From this surface layer the dye

diffuses slowly inwards. The rate of diffusion is much lower than in water, for direct dyes a thousandth or a ten-thousandth of the rate in water.

There is still some doubt as to whether the diffusion follows a simple law, as the evaluation of the experimental results is complicated by the presence of carboxyl groups in the case of cellulose, which, being negatively charged, exert a repulsion on the negatively charged dye ions. For the simple case, the rate of diffusion is proportional to the concentration gradient, and independent of the actual concentration. This does not appear to be the case with direct dyes in Cellophane. However, only a part of the dye within the fibre is freely diffusing: some of it is attached to the cellulose. If allowance is made for this in calculating the concentration gradient within the fibre, more constant values for the diffusion constant are obtained[12].

The very marked change in the diffusion constant with temperature indicates that an activation energy is necessary to bring about diffusion. That is to say, only those molecules with more than a certain amount of thermal energy, the activation energy, can diffuse. Such a diffusion process would follow the usual law for the rate of a chemical reaction—

$$\ln D = C - \frac{E}{RT} \quad \text{or} \quad D = Be^{-E/RT} \qquad \text{(vii)}$$

Thus, the plot of the logarithm of the diffusion constant against the reciprocal of the absolute temperature should be a straight line. From its slope the activation energy can be calculated.

At present there are very few published data from which the above calculation can be made, though it is probable that many results will be available in the near future from work now in progress. Fig. 11 shows some results obtained by

I	...	Human hair, pH 2·04
II	...	Mohair, pH 2·39, 0·1 N. sodium sulphate
III	...	Mohair, pH 2·14, 0·02 N. sodium sulphate
IV	...	Mohair, pH 2·04
V	...	Mohair, pH 1·11
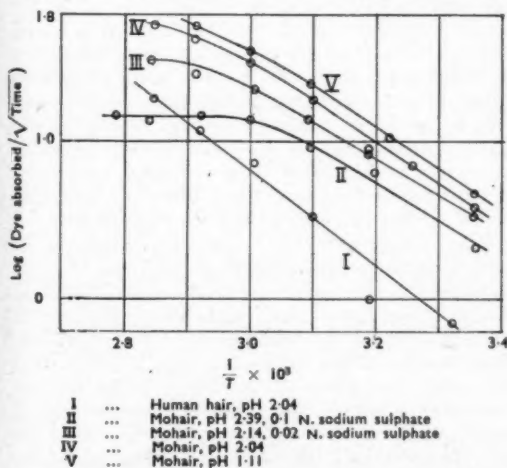
Fig. 11— Relationship between the Logarithm of the Rate of Dyeing and the Reciprocal of the Absolute Temperature T

Gilbert[7] from the work of Speakman and Smith[11]. The dye used was benzeneazo-2-naphthol-6:8-disulphonic acid. The activation energy varied from 23,000 to 28,000 g.cal. according to the fibre

used. At high temperatures the rate of diffusion of the dye in the fibre became sufficiently rapid to compete with diffusion from the solution to the fibre surface. Under these conditions the curves are no longer linear, and equation (vii) does not apply. More vigorous agitation of the dye liquor would extend its validity to higher temperatures.

Very little is known as to why an activation energy is necessary in the dyeing process, or what determines its magnitude. In an ordinary chemical reaction the energy is required to put one or more atoms in an excited state, so that reaction can take place. Dyeing does not require the breaking of main valencies, but the large entropy effect associated with the absorption of the dye by the fibre shows that the dye molecules are subject to considerable restrictions in the fibre as compared with their behaviour in solution. It may be that atomic groupings of the substrate have to be displaced from more stable to less stable configurations to allow the rather large dye molecules to pass. So far as the dye itself is concerned, it seems a general rule that those structural changes which increase affinity also increase the activation energy, and lower the rate of dyeing. This increases the difficulty of redistributing the dye on the fibre and obtaining level dyeings. It would be very useful if the rate of diffusion at high temperatures could be increased, without altering it appreciably at low temperatures. From equation (vii) this would mean increasing the activation energy E and also the constant B. Too little is known about the factors which determine the magnitude of these constants to say whether this is possible.

The fastness of dyeings to wet treatment is probably more dependent on the activation energy than on the affinity. These treatments are usually carried out at the lowest effective temperature, for a limited time, and this time is usually too short to establish equilibrium between the bulk of the fibre and the solution. After the initial loss of dye from the surface of the fibre, the rate of loss depends on the rate at which dye diffuses from the interior to the surface of the fibre.

There are still many problems to be solved. The question of the compatibility of dyes is one which arises in various forms. If two direct dyes with widely different rates of dyeing are dyed on to viscose in a mixture, one will dye the fibre first, to the exclusion of the other. The result is that the colour of the piece changes during dyeing, and the final shade tends to be uneven. This difficulty can be remedied by selecting dyes with approximately the same rate of dyeing. Even so, however, difficulties sometimes arise, which seem to be due to the formation of complexes between the molecules of the two dyes. The absorption spectra of mixtures of direct dyes are not always additive. Another point to bear in mind with direct dyes is that some of them, those of the urea type, are rather easily hydrolysed in a boiling dyebath, with loss of affinity for cellulose.

The incompatibility observed with acid dyes on nylon is probably of a different nature. The acid-combining power of nylon, if combination with

amide groups is excluded, is about 0·035 gram-equivalent per kilogram. This corresponds to about 1·4% of a pure monosulphonic acid dye, and to about 0·7% of a disulphonic acid. This is the reason for the difficulty of obtaining shades on nylon which are both full and fast.

The result of this small combining power is that every basic site on the surface of the fibre is occupied by a dye molecule. If two different dyes are present in the dyebath in equal concentrations, they will not be present on the surface of the fibre in equal proportions unless their affinities are equal. In general this will not be the case. The two dyes will also diffuse into the fibre at different rates, depending on their activation energies of diffusion in nylon. If the two dyes are to be absorbed at equal rates, the product—

Proportion of surface occupied × Rate of diffusion

must be equal for the pair.

Let θ_1, θ_2 be the proportions of the surface occupied by the dyes (1) and (2), and let D_1, D_2 be their diffusion coefficients at the same temperature. Then, if the two dyes are present in the dyebath at equal molecular concentrations, and are of the same valency—

$$RT \ln \frac{\theta_1}{\theta_2} = - (\Delta\mu_1 - \Delta\mu_2) = - \Delta G$$

from equation (vi), and—

$$\ln \frac{D_1}{D_2} = C_1 - C_2 - \frac{(E_1 - E_2)}{RT} = \Delta C - \frac{\Delta E}{RT}$$

from equation (vii).

The condition for compatibility is—

$$\theta_1 D_1 = \theta_2 D_2$$

Hence—

$$\frac{\Delta G}{RT} = \Delta C - \frac{\Delta E}{RT}$$

or

$$\Delta G + \Delta E = RT \, \Delta C$$

For reactions of the same type the constant C varies little in comparison with the activation energy E, so that it is reasonable to put $\Delta C = 0$. The condition for compatibility then becomes—

$$\Delta G + \Delta E = 0 \qquad\qquad \text{(viii)}$$

Hence—

$$G_1 + E_1 = G_2 + E_2 \qquad\qquad \text{(viii}a\text{)}$$

That is, two dyes should be compatible if the algebraic sum of the affinity and the activation energy is the same for both. It seems that for nylon, on which both the activation energy and the affinity of acid dyes is greater than on wool, the condition implied in equation (viii$a$) is not as easily satisfied as on wool.

An effect which is probably of the same nature as the compatibility problem is the resist effect obtained with certain colourless sulphonic acids on wool and nylon. It is well known that chlorination increases the rate of uptake of dyes; indeed, the preparation of wool fabrics for printing by wet chlorination was one of Mercer's inventions. Recently chlorination has been used as a means for reducing the felting power of wool, and for controlling shrinkage. The increase in the rate of dyeing which results can be troublesome, causing unlevel dyeing with milling dyes. The addition of certain complex sulphonic acids, themselves colourless, can reduce the rate of dyeing, presumably by occupying surface sites and not diffusing into the fibre. Wool treated with these compounds can be used with untreated wool to give tone-in-tone effects. On nylon a complete resist is obtained, and this effect can be used in printing.

Some of the substances which give this effect resemble the wetting agents containing a sulphate solubilising group made from petroleum hydrocarbons. The use of these wetting agents in sheep dips might therefore lead to some obscure dyeing problems.

There are many other problems related to the absorption of dyes which are still unsolved. It is well established that acid dyes exert a marked catalytic effect on the hydrolysis of peptide and amide groups in protein fibres[13]. Orange II is about one hundred times as effective as hydrochloric acid, molecule for molecule, in hydrolysing wool. Acid dyes also exert a peculiar effect on undrawn nylon. Above a certain concentration of dye the fibre cannot be drawn; dispersed dyes exert no such effect. Textile printing presents a large field in which dyeing is carried out under rather extreme conditions of salt concentration and temperature, and with very short liquor lengths. Each new synthetic fibre brings its own crop of problems. It is noticeable that the dispersed dyes, where they can be used, seem to give less trouble than dyes solubilised by an ionic group, but unfortunately they do not possess the fastness to washing which is increasingly demanded.

The rate of progress in recent years has been very great, and it seems that a theoretical understanding of most of these problems is possible by the application of existing knowledge. To this extent one of the principal requirements of a theory of dyeing seems possible of achievement, namely the interpretation of all the phenomena of dyeing by the application of established physical and chemical principles. Many of the results may have applications outside the textile field. The two principal materials of the textile industry, wool and cotton, are representative of the two principal structural materials of the animal and vegetable kingdoms, protein and cellulose. It is probable, therefore, that the results of textile research will be useful to the biochemist and the physiologist.

What advantage will an advance in theoretical knowledge bring the dyer? Dyers are often plagued by other people's problems, and blamed for other people's mistakes. More knowledge may enable sources of trouble to be diagnosed more quickly. The remedy will be more easily found, or the dyer will know for certain that there is no remedy within his power. New dyes will be introduced with improved working properties, and the dye manufacturers will pay as much attention to the affinity and dyeing rate of their products as they do now to shade and fastness. The problem of fast and compatible mixtures on many fibres will be solved, and many of the troubles which beset the dyer will be overcome. It is pretty certain, however, that there will be others to take their place. Yet by following the example which John Mercer

set, the application of our scientific knowledge to the dyeing industry, these problems also, in their turn, will yield to us.

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WEST RIDING SECTION

Meeting held at the Great Northern Hotel, Leeds, on 28th February 1950,
Mr. J. M. GOODALL in the chair

The Relationship Between Detergency and Adsorption by the Fibre

K. McLaren

Introduction

One of the most complex processes employed in textile technology is that of detergency, which usually involves the removal of water-insoluble matter from a substrate by the action of aqueous solutions of surface-active compounds, such compounds being those which markedly change the surface properties of water when present in very small amounts. The distinguishing characteristic of surface-active compounds is that they are unbalanced, a molecule of such a compound consisting of two portions— a water-compatible or hydrophilic part and an oil-compatible or hydrophobic part. This characteristic causes inherent instability in aqueous solutions, which is partly overcome by two main effects— the formation of micelles and orientation at an interface; this second factor is responsible for the ability of these compounds to cause wetting, emulsification, and detergency.

Any finite volume of detergent solution usually has a surface in contact with air (or, more precisely, water vapour) and also a surface in contact with the walls of the containing vessel; the region of contact is known as the interface and it is of molecular thickness. The air surface and the surface of the vessel are both more compatible with the hydrophobic part of the molecule than water, and therefore if a molecule is aligned so that the hydrophobic part is adjacent to the air or other surface and the hydrophilic part is in the water, the inherent instability is partly overcome. Surface-active molecules will therefore tend to concentrate at the interface, and this phenomenon is known as *adsorption*.

The importance of adsorption at the many interfaces present when a soiled material is placed in a detergent solution was clearly shown by Adam[1], who, in 1937, studied the removal by a detergent solution of an oil from a wool fibre and observed through a microscope that the oil, which initially wetted the fibre, thus forming a comparatively even layer on it, collected into droplets which were displaced from the fibre by slight mechanical action.

He showed that a maximum detergent effect would occur when—

$$\frac{(w_{sf} - \gamma_s) - (w_{of} - \gamma_o)}{\gamma_{so}} > 1$$

where—

w_{sf} = Work of adhesion of the detergent solution for the fibre
w_{of} = Work of adhesion of the oil for the fibre
γ_s = Surface tension of the detergent solution
γ_o = Surface tension of the oil
γ_{so} = Interfacial tension between the detergent solution and the oil.

From this equation it can be seen that detergency is promoted by—

(1) Low interfacial tension between the detergent solution and the oil
(2) Low surface tension of the detergent solution
(3) High work of adhesion between the detergent solution and the fibre.

Whilst a great deal of work has been done on the importance of interfacial and surface tensions in detergency, there has been very little published relating to the importance of the work of adhesion of the detergent solution for the fibre.

Wool, even in the absence of grease, is not readily wetted by water at temperatures below 100°c.; to achieve a high work of adhesion between the solution and the fibre, the detergent must act as a wetting agent, and adsorption at the fibre–solution interface must occur.

An opportunity to study the importance of adsorption by the fibre was presented by the discovery that a certain ethylene oxide condensate, containing about twenty molecular proportions of ethylene oxide, was of negligible detergent efficiency for wool under normal test conditions although its cotton-detergent efficiency was high. Preston[2] found that the adsorption of a related compound by wool increased in the presence of acid. He thought that the failure of the "20" compound to wash wool was due to insufficient adsorption by the fibre, and that, in the presence of acid, the adsorption should increase with a corresponding

increase in detergency. Preliminary tests showed that efficient detergency did occur in the presence of acid, and it was decided to study the effect on the wool-detergent properties of this compound of factors likely to increase adsorption, and, if possible, correlate these quantitatively by adsorption determinations. The factors studied were the concentration of detergent, the temperature, the pH, and the neutral salt concentration.

Experimental

STANDARD SOILED MATERIAL

Dried commercial botany wool serge was passed quickly through a suspension of 30 g. of lamp black and 15 g. of anhydrous lanolin in 4 litres of white spirit, nipped between rubber rollers, and air-dried.

STANDARD DETERGENCY TEST

A 1·5-g. square of soiled serge is washed with 50 ml. of detergent solution in a conical porcelain vessel immersed in a waterbath so as to maintain a temperature of 50°c. in the vessels. Mechanical agitation is provided by frequent vigorous stirring by hand. After 15 min. the patterns are rinsed in water at 50°c. and again in cold water, and then dried.

DETERGENT EFFICIENCY

The amount of light reflected from the washed pattern was measured photoelectrically, the galvanometer scale being adjusted to read 0 for the soiled and 100 for the unsoiled material; readings were taken in two directions on both sides of the cloth. Each point on the graphs (Fig. 2–13) was obtained from only one detergency experiment.

ADSORPTION

100 ml. of detergent solution is maintained at the required temperature in a cylinder containing 3 g. of cloth (previously conditioned at 65% R.H. and 22°c.), as shown in Fig. 1. The upper end of the rod is attached to a vertically oscillating lever, and the movement of the cloth forces the solution continually through it; the cylinder is immersed in a thermostat. After 15 min. the cloth is removed, and the residual concentration of detergent estimated by precipitation with phosphomolybdic acid[3].

A similar experiment is conducted in the absence of wool to eliminate changes in concentration due to extraneous causes, such as adsorption on to the apparatus and loss of water by evaporation. From any difference in residual concentration the adsorption of detergent by the wool can be calculated.

To determine if this method was sufficiently sensitive to detect the small changes in concentration expected in such a short period of time, experiments were conducted with another ethylene oxide condensate of excellent wool-detergent properties under normal conditions, whose adsorption by wool must obviously be sufficient; the results are given in Table I. Subsequent results were similarly obtained, i.e. from the mean weight of six determinations in the presence of wool and six in its absence.
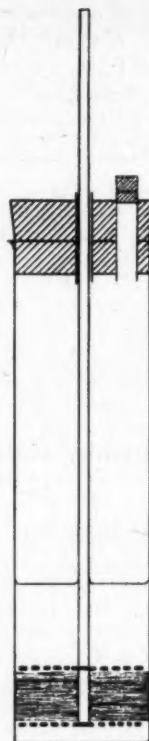

FIG. 1

TABLE I

Initial concentration of detergent 0·05%
Temperature ... ... 70°c.
Weight of precipitate (g.) obtained from 50 ml. residual solution—

	Wool absent	Wool present
	0·0755	0·0636
	0·0750	0·0618
	0·0750	0·0618
	0·0705	0·0568
	0·0729	0·0612
	0·0754	0·0624
Mean	0·0741	0·0611

Calculation

0·0741 g. Precipitate = Detergent concentration of 0·05%

$\therefore$ 0·0611 g. Precipitate = Detergent concentration of $\dfrac{0.05 \times 0.0611}{0.0741}$
$\qquad = 0.0412\%$

3 g. Wool has therefore absorbed 0·0500 − 0·0412
$\qquad\qquad = 0.0088$ g. Detergent

Adsorption = 0·35 g. per 100 g. dry wool.

Notes

(1) It is assumed that the residual concentration of detergent in the absence of wool is equal to the initial concentration; the slight change occurring does not appreciably affect the calculated adsorption.

(2) No allowance has been made for the change in concentration due to the adsorption of water by wool. The saturation regain of wool at 22°c. is 34%[4], and the standard regain of woollen and worsted cloth 16%[5]. The wool will therefore adsorb 18% = 0·54 ml. water, which will alter the precipitate weight by only 0·0003 g. At higher temperatures the adsorption of water by wool is much less[6], and therefore its effect on the adsorption of detergent can be ignored.

(3) A correction must be applied if any soluble matter extracted from the wool is precipitated by any of the reagents— hydrochloric acid, barium chloride, and phosphomolybdic acid— used in the estimation of detergent concentration. Unfortunately it is not sufficient merely to carry out a blank determination in the absence of detergent, as the wool is not wetted under such conditions. All the wetting agents tried were precipitated by the reagents used, and it was necessary to moisten the wool first with a water-miscible solvent; alcohol was unsatisfactory, as soap was extracted and precipitated, but acetone appeared to be satisfactory. Where it was necessary to apply such a correction, the abbreviation "corr." appears after the weight of precipitate. Such corrections were also necessary on purified wool, the degradation

detergency (70%) occurs at the higher temperature.

That some adsorption occurs is probable, as the wool is, in all cases, wetted by the solutions but not by water; this adsorption must be less than 0·05 g. per 100 g. dry wool, the sensitivity of the method assuming that a difference of 0·0025 g. in mean precipitate weights can be reliably detected.

2. EFFECT OF P_H

(a) Detergency

Fig. 3 shows the effect on the detergent properties of a 0·03% solution of additions of sulphuric acid, the concentration of acid being expressed on the volume of solution; Fig. 4 shows the same results expressed as a function of the final pH of the detergent solution. These curves show that—

FIG. 2

—O— 80°C.   —X— 90°C.
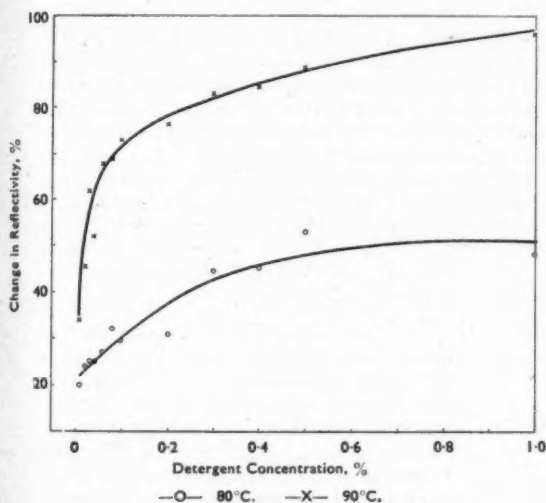
products of keratin being precipitated and frequently turning the colour of the supernatant liquid from yellow to green.

Results and Discussion

1. EFFECTS OF TEMPERATURE AND DETERGENT CONCENTRATION

(a) Detergency

Fig. 2 shows the effect of increasing the concentration of detergent at 80° and 90°c.; at lower temperatures there is negligible detergent action even in solutions of 20% concentration.

(b) Adsorption

The results of adsorption determinations are given in Table II.

TABLE II

Temperature °c.	Initial Detergent Concentration (%)	Mean Weight of Precipitate— Without wool (g.)	With wool (g.)
70	0·025	0·0398	0·0393
	0·050	0·0840	0·0845
	0·050	0·0813	0·0828
	0·100	0·1681	0·1681
90	0·100	0·1664	0·1666 (corr.)

These results show that no adsorption detectable by this method occurs at 70° or 90°c., but that good

FIG. 3

—△— 40°C.   —+— 65°C.
—O— 53°C.   —●— 77°C.
—×— 58°C.   —□— 87°C.

FIG. 4

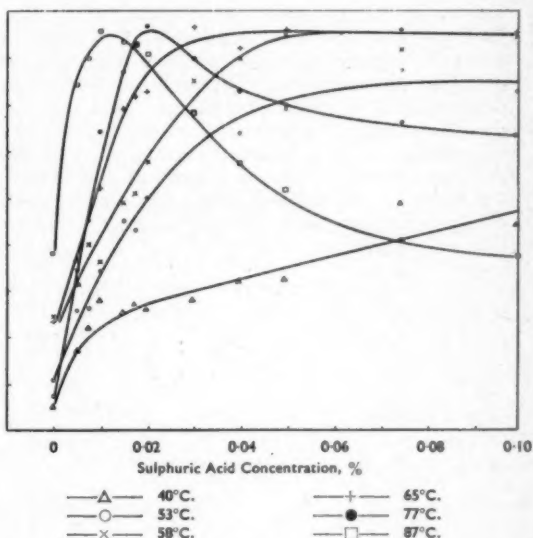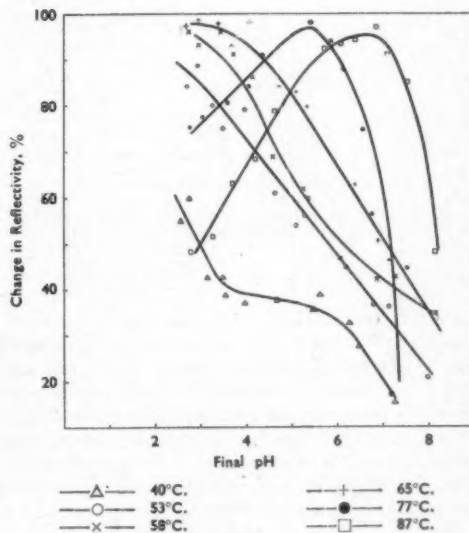—△— 40°C.   —+— 65°C.
—O— 53°C.   —●— 77°C.
—×— 58°C.   —□— 87°C.

(i) At temperatures up to ca. 65°c., detergent efficiency increases with increasing concentration of acid up to a maximum and remains constant

(ii) At higher temperatures detergent efficiency reaches a maximum and then decreases

(iii) The acid concentrations at these maxima are lower the higher the temperature

(iv) The slope of the initial increase is steeper the higher the temperature

(v) The decrease in detergent efficiency when the optimum acidity is exceeded is greater the higher the temperature.

Each of these observations can be satisfactorily explained by assuming that the addition of acid causes an increase in adsorption by the fibre, the increase being greater at higher temperatures. The eventual decrease in detergency at higher temperatures could then be due to excessive adsorption, which Adam[1] has shown may cause a decrease in detergency if the residual amount of free detergent in the bath is too low to retain the soil, which has already been removed, in suspension. If this happens, redeposition may occur.

FIG. 6

being equal. This effect is shown in Fig. 6; the solution used (0·02% detergent, 0·02% H_2SO_4) contained more acid than was required for optimum detergency in 15 min. at 90°c. It would appear that sufficient adsorption by the fibre for reasonable detergency occurs in one minute only, and the detached soil is suspended in the solution by a protective layer of adsorbed detergent; the affinity of the fibre for the detergent is, however, greater than that of the soil, and the latter is slowly deprived of its protective layer and becomes redeposited.

An interesting anomalous series of results was obtained when the effect of detergent concentration was studied at varying acid concentrations and various temperatures. Fig. 2 showed that, in the absence of acid, an increase in detergent concentration caused an increase in detergency if the temperature were high enough; Fig. 7–11 show the effect of detergent concentration at different concentrations of acid. The results can be summarised as follows—

(i) Up to 0·015% acid, an increase in detergent concentration causes an increase in detergency

(ii) When the acid concentration reaches 0·02% an increase in detergent concentration causes—

(α) a decrease in detergency at 50°c.

(β) an increase followed by a decrease at 60° and 70°c.

(γ) an increase in detergency at 75° and 80°c.

FIG. 5

Confirmation of this is given in Fig. 5, in which it is observed that the decrease in detergent efficiency at high concentration of acid does not occur if the initial concentration of detergent is sufficiently high, viz. ca. 0·10%. Great adsorption by the fibre is therefore not in itself a cause of poor detergency, which results only if dangerous depletion of the detergent bath occurs. Adam discovered the excessive adsorption–depletion effect by observing that sometimes less soil was removed during a long wash than during a short one, other factors

(iii) At higher acid concentrations, similar behaviour occurs, but the temperature at which the increase–decrease phenomenon is first noticed is lower the greater the acid concentration.

No explanation of this anomalous effect can yet be given; it will be seen later that the effect is not due to an inherent characteristic of wool.

(b) Adsorption

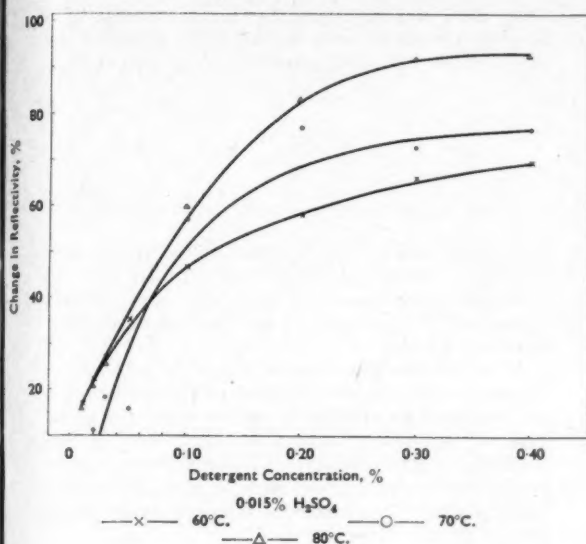The results of adsorption determinations are given in Table III.

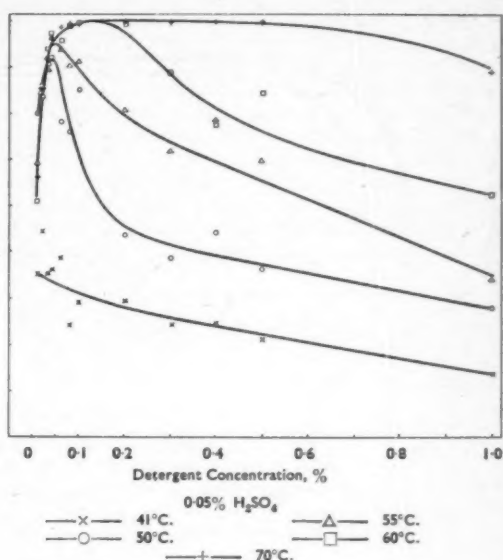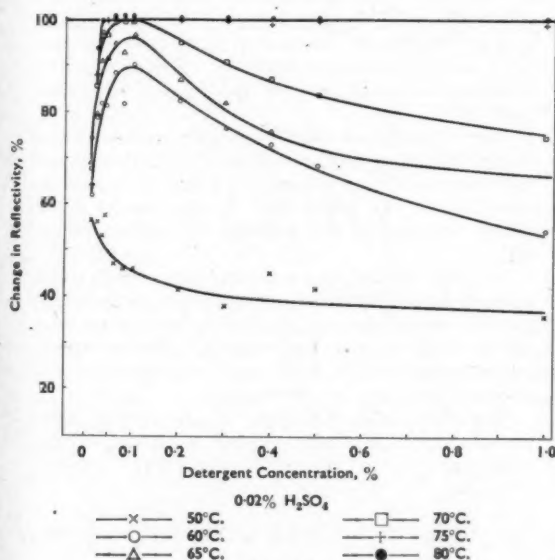0·015% H₂SO₄

—×— 60°C.   —○— 70°C.

—△— 80°C.

Fig. 7

0·05% H₂SO₄

—×— 41°C.   —△— 55°C.

—○— 50°C.   —□— 60°C.

—+— 70°C.

Fig. 9

0·02% H₂SO₄

—×— 50°C.   —□— 70°C.

—○— 60°C.   —+— 75°C.

—△— 65°C.   —●— 80°C.

Fig. 8

0·25% H₂SO₄
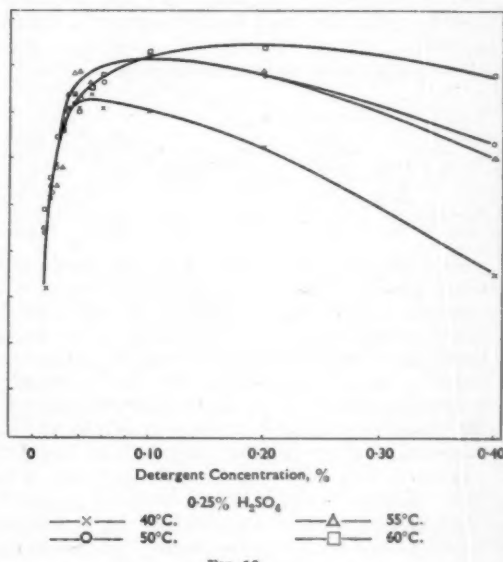
—×— 40°C.   —△— 55°C.

—○— 50°C.   —□— 60°C.

Fig. 10

TABLE III

Temp. (°C.)	Initial Detergent Concentration (%)	Acid Concentration (ml. N·HCl* per 100 ml. solution)	Final pH	Final Detergent Concentration (%)	Adsorption (g. per 100 g. dry wool)
70	0·05	0·0	6·60	0·050	[0·00
		1·0	3·50	0·047	0·12
		5·0	2·51	0·044	0·21
90	0·10	0·0	6·65	0·100	0·00
	0·03	0·5	4·34	0·011	0·70
		1·0	3·27	0·007	0·84

* Hydrochloric acid had to be used, not sulphuric acid as was used in detergency, as the latter is precipitated by the reagents employed in the estimation.

These results confirm the prediction made from a study of the detergency results, viz.—

(i) As the acid concentration increases, the adsorption increases

(ii) The increase in adsorption is greater at the higher temperature

(iii) The decrease in final detergent concentration at high temperatures and high acid concentration is sufficient to cause excessive depletion of the bath.

In view of the non-ionic character of this detergent, it is somewhat surprising that its adsorption by wool should be so sensitive to changes in pH. In order to determine if this were due to wool itself or to one or other of the impurities present in commercial cloth, adsorption determinations were made on raw wool purified by washing in water at

0·25% H₂SO₄

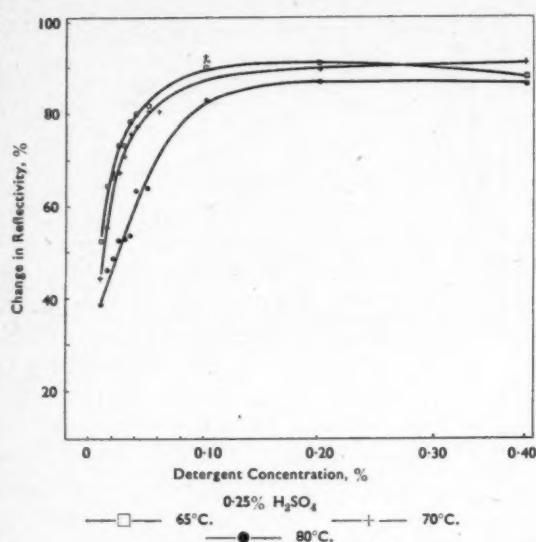——□—— 65°C.   ——+—— 70°C.

——●—— 80°C.

FIG. 11

40°c., drying, extracting with ether and alcohol in a Soxhlet extractor, and finally repeatedly washing in distilled water. The results are given in Table IV, together with comparable results for serge.

TABLE IV

Material	Temp. (°c.)	Initial Detergent Concentration (%)	Acid Concentration (ml. N-HCl per 100 ml. solution)	Final pH	Final Detergent Concentration (%)	Adsorption (g. per 100 g. dry wool)
Pure wool	70	0·10	1·0	2·50	0·098	0·07
Serge ...	70	0·05	5·0	2·51	0·044	0·21

At equal pH values, therefore, the commercial serge adsorbs three times as much detergent as pure wool even from a solution of only half the initial concentration, and therefore it is obvious that one of the impurities present in commercial serge is mainly responsible for the increase in adsorption observed. It was found that removal of the grease present by extraction with ether did not appreciably alter the adsorption values, but serge extracted with ethyl alcohol adsorbed very much less; clearly, soap is the responsible impurity. Confirmation of this was obtained by pretreating purified wool with sodium oleate; the adsorption of detergent by this wool under acid conditions is given in Table V, together with comparable results for serge.

TABLE V

Material	Temp. (°c.)	Initial Detergent Concentration (%)	Acid Concentration (ml. N-HCl per 100 ml. solution)	Final pH	Final Detergent Concentration (%)	Adsorption (g. per 100 g. dry wool)
Wool treated with sodium oleate ...	90	0·03	7·5	3·29	0·004	1·02
Serge... ...	90	0·03	1·0	3·27	0·007	0·84

It is suggested that the mechanism by which relatively large amounts of detergent are adsorbed by soap-containing wool under acid conditions is initially the conversion of the soap to its free fatty acid and subsequently the combination of free fatty acid and detergent by the formation of a hydrogen bond between the hydroxyl group of the acid and the ether oxygen of the detergent—

$$C_{17}H_{35}—C=O$$
$$|$$
$$O$$
$$|$$
$$H$$
$$\uparrow$$
$$—CH_2·CH_2·O·CH_2·CH_2—O—CH_2·CH_2·O·CH_2·CH_2—$$
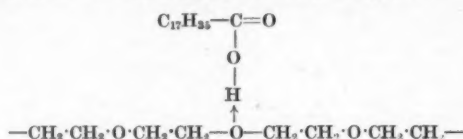
The small adsorption by pure wool under acid conditions (Table IV) may similarly be due to hydrogen bond formation, the $-NH_3^+$ and $-COOH$ formed in the presence of acid acting as proton-donating groups.

It is not thought that this type of adsorption normally occurs when ethylene oxide condensates are employed as wetting agents for wool; the usual type of adsorption occurs by alignment of the molecules so that the hydrophobic portion is close to the hydrophobic wool surface and the hydrophilic portion (in this case the ethylene oxide chain) protrudes into the water.

The discovery that soap in commercial wool is mainly responsible for the increase in adsorption at low pH values immediately suggests that it is also responsible for the observed effects on detergency. The small increase in adsorption by pure wool eliminates any possibility of a decrease in detergent efficiency due to depletion of the detergent bath.

The difficulty of purifying large quantities of serge prevented the repetition of the detergency tests on soap-free wool, but with the small amount available it was found that no increase in detergency occurred in the presence of acid at 60° or 90°c.

Preston[3] showed that a related compound, which possessed excellent wool-detergent properties under normal conditions, was ineffective in acid solution owing to the excessive adsorption–depletion effect; on soap-free soiled wool, acid additions do not materially reduce its efficiency.

The anomalous detergent concentration effect already mentioned must therefore be due to the presence of soap; the mechanism of the effect is unknown.

3. EFFECT OF SODIUM CHLORIDE CONCENTRATION

(a) Detergency

Fig. 12 shows the effect of salt concentration on the detergent properties of a 0·03% solution. These curves show that—

(i) An increase in salt concentration causes an increase in detergency

(ii) At temperatures above 40°c., this initial increase in detergency is followed by a decrease

(iii) The higher the temperature the lower is the optimum salt concentration.

The general similarity between the shapes of these curves and those for acid addition (Fig. 3) naturally suggests that the same cause is operating: i.e. that an increase in salt concentration causes an increase in adsorption by the fibre, which is greater the higher the temperature, and if this results in depletion of the bath, redeposition will cause a
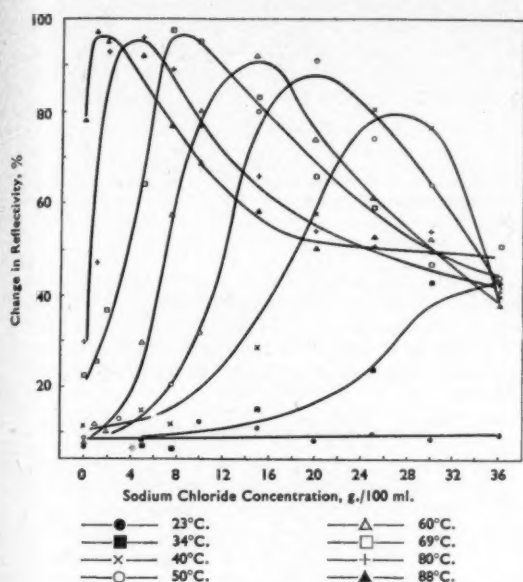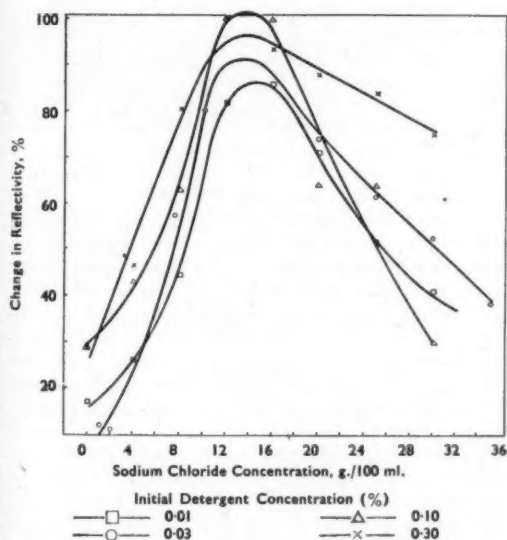
FIG. 12

FIG. 13

these points was from a single determination only, the scatter of the points is considerable. The most obvious feature of Fig. 14 is the sudden increase in adsorption at a concentration of 11% salt. The cause of this was visible during the adsorption experiments; solutions with a salt concentration higher than 11% were seen to be cloudy, but the turbidity disappeared during the course of the adsorption. Clearly, precipitated detergent was being removed from the solution by filtration by the wool rather than adsorption. In Fig. 15, the
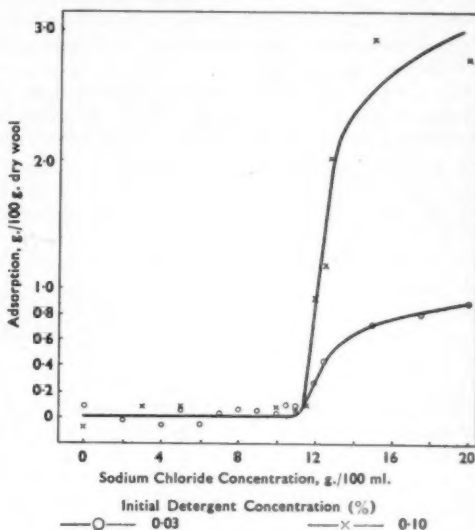

FIG. 14

reduction in detergent efficiency. This reduction would be expected not to occur if the initial detergent concentration were sufficiently high, but Fig. 13 shows that it occurs even at 0·3% at 60°c.; therefore, either exceptionally high adsorption occurs in this region or some other mechanism is responsible.

(b) Adsorption

The effect of salt concentration on adsorption is more clearly shown in a graph than a table, and Fig. 14 shows the adsorption plotted against sodium chloride concentration for initial detergent concentrations of 0·03% and 0·10% at 70°c. Since each of
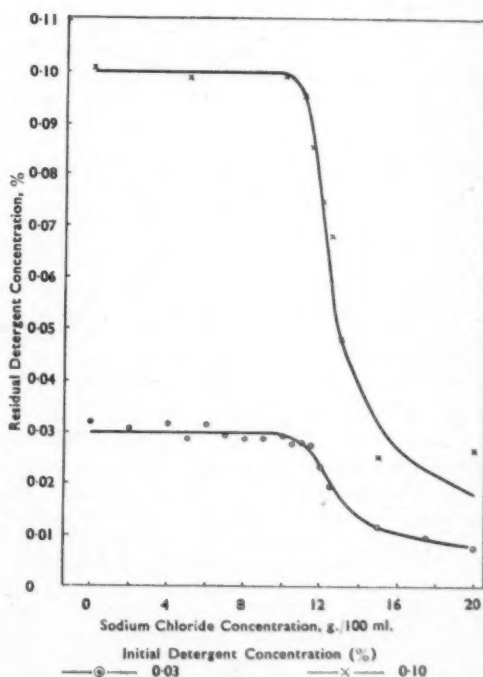

FIG. 15

same results are shown expressed as residual detergent concentration; it can be seen that dangerously low detergent concentrations occur even when the initial concentration is high.

The maximum amount of salt which can be employed without causing clouding at 70°c. is approx. 10%, and this is about the optimum for detergency as shown in Fig. 12. This relationship holds over a wide range of temperatures, as shown in Fig. 16, in which the optimum salt concentrations from Fig. 12 and the minimum salt concentrations necessary to cause clouding are plotted against temperature. The inter-relationship between adsorption, clouding, and detergency at 70°c. is shown in Fig. 17.

There does not appear to be any increase in adsorption to account for the initial increase in detergency, i.e. at salt concentrations below the

minimum necessary to cause clouding. This was confirmed by determining the adsorption by the usual method at a salt concentration just below the cloud point; the results are given in Table VI.

<table>
<tr><td colspan="4" align="center">TABLE VI</td></tr>
<tr><td>Temperature</td><td>...</td><td>...</td><td>70°c.</td></tr>
<tr><td>Initial detergent concentration</td><td>...</td><td></td><td>0·10%</td></tr>
<tr><td>Sodium chloride concentration</td><td>...</td><td></td><td>9·0 g./100 ml</td></tr>
<tr><td>Mean weight of precipitate—</td><td></td><td></td><td></td></tr>
<tr><td>Without wool ...</td><td>...</td><td>...</td><td>0·1622 g.</td></tr>
<tr><td>With wool ...</td><td>...</td><td>...</td><td>0·1623 g.</td></tr>
</table>

The effect of salt on the detergent properties is not due to the presence of soap in the wool; similar results were obtained on soap-free soiled wool. In the presence of salt there are no anomalous detergent concentration effects as occur in the presence of acid.

Summary and Conclusions

The effect of four variable factors—temperature and detergent, acid, and salt concentration—on the wool-detergent properties of a specific non-ionic surface-active compound has been studied in detail; the effect of each on the adsorption of detergent by the fibre has also been determined. It has been shown that—

(1) Increasing the temperature from the normal wool detergency temperature of 50°c. to 80–90°c. causes an increase in detergent efficiency. At these temperatures an increase in detergent concentration also improves detergency. No adsorption of detergent by the fibre could, however, be detected, although it is probable that, as the fibre was wetted by solutions of the detergent, some adsorption must have occurred. This must be less than 0·05 g. per 100 g. dry wool.

(2) The effect of adding acid to the detergent solution is to cause an increase in detergency; at high temperatures, when a certain acid concentration is exceeded, the detergent efficiency is reduced. Both these effects are accompanied by an increase in the adsorption by the substrate as the acidity increases. The decrease in detergency is due to excessive adsorption, which reduces the concentration of free detergent below that necessary to retain already detached soil in suspension; redeposition of soil then occurs. The major part of the increase in adsorption at low pH values is due to the presence of soap in commercial wool and, if this is removed, additions of acid no longer cause any improvement in detergent efficiency. It is thought that the mechanism involved in adsorption is first the conversion of soap to its free fatty acid, and subsequently the combination of detergent and fatty acid by means of hydrogen bond formation between the hydroxyl group of the acid and an ethereal oxygen atom in the detergent.

(3) Adding sodium chloride to the detergent solution causes an improvement in detergent efficiency up to the concentration where precipitation occurs; this concentration is lower the higher the temperature. At higher concentrations, the detergent efficiency falls. No adsorption by the fibre could be detected at salt concentrations below the critical value.

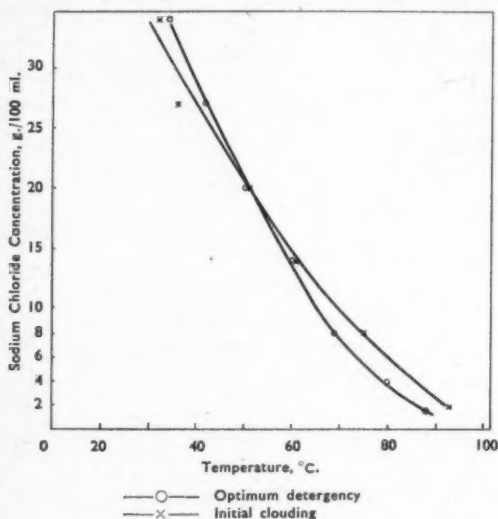The failure of this detergent to wash wool under normal conditions cannot be due to insufficient
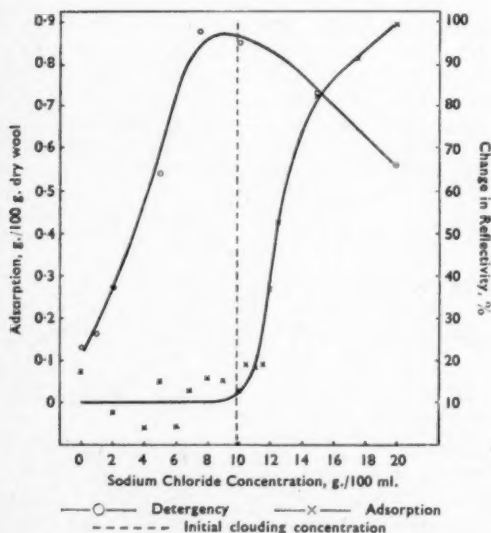

FIG. 16

FIG. 17

adsorption by the fibre; at higher temperatures and in the presence of salt, excellent detergent efficiency occurs, but no adsorption could be detected. Some adsorption probably occurs under normal conditions, however, because water alone does not wet wool in 15 min. at temperatures much below 100°c., yet in every case, complete and rapid wetting occurred in the presence of detergent whether accompanied by soil removal or not. Efficient detergency may not, therefore, require any greater adsorption by the fibre than occurs in wetting.

On the other hand, the increase in detergency caused by additions of acid is accompanied by an increase in adsorption by the soap present in the fibre, and if this is removed prior to applying the soil, no improvement in detergent efficiency occurs.

It is tempting, therefore, to conclude that, in the case of acid additions, the increase in adsorption causes the improvement in detergency, as expected from Adam's equation; some other mechanism, however, must be responsible for the increase in detergency at higher temperatures and in the presence of salt.

The author wishes to acknowledge the valuable assistance rendered by Dr. C. Preston during this investigation.

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Discussion

Dr. H. R. HIRSBRUNNER: In the textile trade the oiling of wool with mineral oil or blended oil of high mineral oil content is associated with difficulties. This is strikingly shown by results obtained by scouring woollen fabrics, containing 10% of a blended oil (80% mineral oil + 20% oleic acid), in a soap liquor. Laboratory tests suggest that this blend would be an adequate method of handling the problem of mineral oil removal[7]. This, however, is unfortunately not the case; Goodings and Marshall[8] state that in industrial mill practice disturbing factors arise which upset any such simple procedure.

Is Mr. McLaren in a position to give an explanation for these most contradictory results? In all industrial practice more or less variable factors, such as the presence of relatively small quantities of natural fatty acids and the hardness of water, have a very pronounced effect upon the removal of mineral oil. Nevertheless, I am inclined to believe that the cause of the poor removal in large-scale operation lies also in a slight adsorption of

soap by the greasy wool, whilst clean wool must show a relatively high amount of adsorption of soap and promote, therefore, the scouring process.

Mr. McLAREN: I regret that I cannot suggest any explanation for these results. It is, however, true that clean wool does adsorb relatively large quantities of soap, the alcohol extract of commercial wools (customarily attributed to soap) being about 1%; but the work just described suggests that adsorption greater than that necessary to cause wetting of the fibre is not essential, and that quantitatively this amount is very low (< 0·05%).

Mr. R. K. FOURNESS: Have experiments been done to determine the detergent action of ethylene oxide condensates *in neutral solution* on wool to which has been added a small amount of free fatty acid? The results of such experiments may perhaps confirm or otherwise the theory that the increased detergent action, noted when mineral acid is added to the detergent solution, is due to the hydrogen bonding said to occur between the non-ionic detergent and the fatty acid liberated by the mineral acid from the soap residues in the wool.

Mr. McLAREN: One experiment was carried out on the lines suggested: commercial serge was soiled with grease and carbon, the lanolin normally used being replaced by an equal weight of oleic acid. Excellent detergent efficiency occurred with 0·05% detergent at 50°c. under neutral conditions. Although this experiment is not conclusive, as the soil is now different, it undoubtedly confirms the views suggested.

Mr. H. JENNISON: Would dilution of the bath tend to maintain the upward curve as shown, or would it produce a more rapid absorption of soil by the fibre? This is a very important point for consideration in the practical application of any scouring reagent.

Mr. McLAREN: It is difficult to say what would be the effect of dilution on the depletion–redeposition curve: dilution would probably reduce the rate of absorption of detergent by the fibre, a factor which would tend to reduce redeposition; but it might also reduce the stability of the suspended soil, a factor which would have the opposite effect. In practice, however, the conditions of scouring with non-ionic detergents are such that excessive absorption will not occur, and therefore dilution will affect the emulsion or suspension stability only. Dilution of the scouring bath should therefore be gradual, and with water at the same temperature as the bath to ensure stability.

Mr. H. JENNISON: Would the "20" detergent scour in an acid bath?

Mr. McLAREN: The scouring efficiency of the "20" compound in acid solutions is caused by the presence of soap, the results being very sensitive to changes in pH and temperature. These factors would have to be controlled to such fine limits that such a scouring method would be quite impracticable. There is, however, another ethylene oxide condensate which was specially prepared as an acid dyebath scouring agent, and this product is commercially available.

COMMUNICATIONS

Radio-frequency Drying of Textile Fabrics

P. ALEXANDER and G. A. MEEK

An apparatus for studying the drying of textile fabrics by high-frequency (dielectric) heating is described. Rate-of-drying curves for thirteen different textile materials, together with measurements of temperature and power consumption, are shown. With every material examined the drying curve shows a discontinuity and the rate of drying decreases at a certain moisture content, which in most cases approximates closely to the reported figures for saturation regain of the respective fibres. The water held by fibres at this moisture content is not free and has anomalous electrical properties. The practical advantages of high-frequency drying are discussed.

Introduction

Drying may be defined as the removal of any volatile substance by the application of heat energy. There are five generally recognised methods of drying— conduction, convection, radiation, vacuum, and radio-frequency. For textile drying the first two are almost universally employed, and are represented by the cylinder process and the oven process respectively. The former is cheap and efficient, but imparts a harsh handle, particularly to wool, whereas the oven process is slower and uses more fuel, but gives softer materials. Both methods suffer from the disadvantage of requiring some form of intermediate heat storage, e.g. superheated steam, and are not readily controllable. Radiant heat, supplied by electrical infra-red elements or by gas-fired radiators, is a very effective method of removing the last traces of moisture and is best employed in conjunction with a convection oven. It is an expensive method, but requires no intermediate heat storage, can be controlled instantaneously, and, because of the high rates of heat flow, the equipment is small and drying times are short. High-frequency or dielectric drying, which forms the subject of this paper, has, in addition to all the advantages of radiant heat drying, the great merit of generating the heat within the body of the material itself. The heating does not involve any transfer mechanism, and is therefore largely devoid of temperature gradients from the outside to the inside of the material, since the thermal conductivity of the material does not affect the supply of heat. In fact, during dielectric drying the outside is usually at a lower temperature than the inside because of greater heat losses to the environment.

Relatively little work has been published on the use of high-frequency electric (radio-frequency, R.F.) fields for drying, although the principle has been known for some years. The generation of R.F. power has been well studied in the past by radio engineers, who have struggled against the heating effects. A detailed monograph[1] dealing with the whole field of R.F. heating has recently been published in America. Morozov[2] in 1938 investigated the drying of cotton fabrics in an R.F. field, and Mann, Ceaglske, and Olson[3] in 1949 studied the dielectric drying of trays of sand.

The basic principle of this method of drying is that no electrical condenser or capacitor returns on discharge all the electrical energy expended in charging it, the remainder reappearing in the material of the dielectric in the form of heat. The rate of transfer of energy to the dielectric will be seen to be proportional both to the frequency of charging and discharging, and to the amount of electrical energy transferred to it during each cycle, since an imperfect dielectric retains a constant proportion of energy each time it is charged and discharged. It can be shown that the power in watts W developed and dissipated as heat in a cubic centimetre of a material of dielectric constant ε subjected to an alternating field of frequency f cycles per second at E volts is given by the formula—

$$W = 5 \cdot 55 \times 10^{-13} E^2 f \varepsilon \tan \delta$$

where the quantity $\tan \delta$ is the *power factor* of the material. The product $\varepsilon \tan \delta$ determines the proportion of electrical energy retained as heat per cycle, and is known as the *loss factor*. The power factor $\tan \delta$ can be considered as a measure of the conductivity of the system at the frequency used.

It would appear at first sight that a good non-conductor of electricity such as a textile fabric would be incapable of absorbing electrical energy, and this is the case for direct, but not for high-frequency alternating, currents. An electric current is defined as the transport of charge from one point to another under the influence of an electric field, and thus periodic displacement of bound charges by a field which is cyclically reversing its polarity constitutes a current. Consequently, substances which are insulators for direct current can carry alternating current, and since all known substances offer resistance to the path of a current at ordinary temperatures, a proportion of the electrical energy will be dissipated in the body of the substance as heat.

There are three types of charge which are polarised in an electric field— molecular dipoles, which may be permanent or induced by the exciting field; atomic charges; and lastly electronic charges. The first have a natural frequency of oscillation in the wireless wave range, the second in the infra-red, and the last in the ultra-violet and X-ray region. We are concerned with the motion of molecules produced by the oscillation of dipoles. Atomic and electronic oscillations do not contribute to the heating, for the power absorbed will be greatest when the time of oscillation (relaxation period) of the molecule is the same as the time for one half-cycle of the exciting field. This optimum frequency is not critical even for pure substances[4], and for a mixture such as wet wood[5] the loss factor changes only by a factor of 2 over the range 1–600
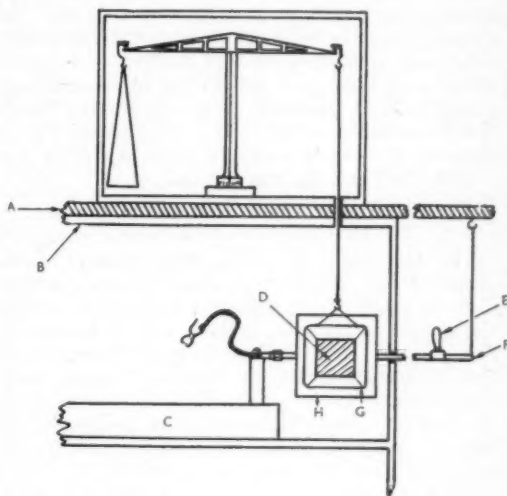
megacycles per second. For this work, an oscillator working at 41 megacycles per second was chosen, since this is near the limiting frequency for efficient operation of a self-excited valve oscillator, and also close to the value for optimum power absorption in the systems studied.

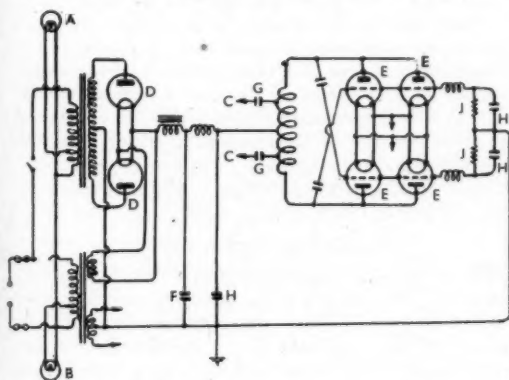## Experimental Procedure

1. APPARATUS

Samples of wet textile materials of known moisture content were dried in a homogeneous alternating electric field of 41×10^6 cycles per second, and the rate of loss of water, the temperature of the sample, and the power absorbed by it were recorded. The high-frequency oscillator used consisted of a 250-watt output generator of the double-ended, series-fed Hartley type employing four triode valves in parallel push–pull (see circuit diagram, Fig. 1) each with a rated anode dissipation of 50 w. and delivering in the class C circuit used about 75 w. of R.F. power each. The anode circuit power was obtained from a power pack capable of supplying 1250 v. D.C. at 0·5 amp. Heater current for the rectifiers and oscillator valves was obtained from a separate transformer. The oscillator and the power pack were in two units adapted from a commercial dielectric heater marketed by the Arc Manufacturing Co. The two units were housed in a cupboard under a bench (Fig. 2), the oscillator being on the upper shelf. The R.F. output from the generator was tapped off the tank coil by means of

A	...	Red pilot	F	...	4 μF.	
B	...	Green pilot	G	...	5 pF.	
C	...	Output clips, 1250 v.	H	...	100 pF.	
D	...	Osram U 19	J	...	4000 ohms	
E	...	Osram Det 12				

Fig. 1—Circuit Diagram of Radio-frequency Generator

large bulldog clips, and was fed through two 5-pF. (5×10^{-12} F.) isolating condensers, the purpose of which was to remove the dangerous 1250 v. D.C. component, into a Lecher wire system provided with two 6-in. square vertical aluminium condenser plates. The system was tuned by shunting with a movable short-circuiting bar provided with a thermocouple ammeter. The Lecher wires consisted of two pieces of $\frac{5}{16}$ in. (outside diameter) copper tubing each one-quarter wavelength (180 cm.) long and permanently shorted at the ends by a semi-circular piece of copper tubing. The frequency used

was determined by the inductance of the main tank coil in parallel with the grid condensers and the associated stray circuit capacities, and was measured with a small absorption wavemeter which had been calibrated from a standard signal generator. The frequency varied by no more than 2% on changing the power output of the oscillator from zero to its maximum value.

A	...	Bench	E	...	Shorting bar
B	...	Cupboard	F	...	Lecher wires
C	...	Oscillator chassis	G	...	Glass frame
D	...	Sample	H	...	Condenser plates

Fig. 2— Diagram of Apparatus

The textile samples used were cut from fabric which had been made on a circular knitting machine, several thicknesses being folded into a pad about 8 cm. square, which was then sewn up the open edges with a thread of the same material. This pad was sewn to the corners of a square frame made of 3 mm. Pyrex glass rod, which was suspended between the plates of the load condenser by two nylon threads of opposite twist passing upwards through a hole in the bench. The upper ends of the threads were attached by sealing wax to a small copper wire hook which was hung on to the stirrup of a long-beam type of chemical balance, whose sensitivity had been reduced so as to decrease the time of swing. The other arm of the balance carried an ordinary scale-pan and also a small lead weight suspended from the stirrup to counterbalance the weight of the suspension for the sample. The sample was maintained in a homogeneous electric field by reducing the amplitude of swing of the balance.

The following procedure was followed when carrying out a determination— An accurately weighed sample of approx. 20 g. dry weight was sewn into the frame, wetted out in distilled water containing an anionic wetting agent, rinsed several times in distilled water, and finally gently squeezed by hand to remove excess water. The frame was then attached to the lower end of the suspension by a hook and swivel, and inspected to ensure that it

was clearing the condenser plates. The sample was counterbalanced and its moisture content determined, and the oscillator switched on and brought to the required power level by adjusting the position of the shorting bar across the Lecher wires. A rate-of-drying curve was obtained by periodically removing weights and noting the times when the balance pointer swung through its centre point. The power input as shown by the input meter was kept constant by adjusting the shorting bar. With wet textile materials the power-absorbing capacity decreased sharply at a certain moisture content, so that power input could no longer be kept constant. When no further loss in weight occurred, or when the temperature rise in the sample became excessive, the generator was switched off and the run terminated.

2. TEMPERATURE MEASUREMENT

The measurement of the temperature of the sample during the drying process presents a very difficult problem, since any object introduced into the sample will heat up in the R.F. field owing to its own losses. In a mercury-in-glass thermometer, for example, heat will be dissipated owing to dielectric losses in the glass and to eddy currents in the mercury, and the temperature indicated will bear no relation to the temperature of its surroundings. After detailed investigation it was decided to use a thermocouple of very small physical dimensions, so as to allow any heat which was generated in it to be dissipated quickly. Furthermore, a thin couple has a very quick response to temperature changes. The major difficulty was the induction of eddy currents in the junction from stray pick-up in the leads, and this was overcome by making the leads spiral (i.e. of high inductance) and by interposing suitable condensers to act as an electric filter. The actual junction used consisted of a 40 S.W.G. constantan wire soldered to a 38 S.W.G. copper wire sheathed in a very thin glass tube closed at one end. This probe could be inserted in the sample, the temperature being read on a calibrated galvanometer. The cold junction, also sheathed in a glass tube, was immersed in a beaker containing melting ice. Since the thermojunction leads impeded the swing of the balance, a separate but identical run had to be carried out after the drying run in order to obtain the temperature.

Results

The results obtained with thirteen different types of fibres are shown in Fig. 3–17. In each case the three variables— moisture content, temperature, and power consumption by the anode circuit of the oscillator— have been plotted against time.

All the materials examined showed a similar moisture content–time graph, which can be divided into three parts— the warming-up period, the constant-rate period, and the decreasing-rate period. Fig. 3, showing the drying of knitted wool fabric, represents a typical experiment, and the general features of R.F. heating can be discussed by considering this example.

Within the first two minutes, the temperature of the sample and the rate of drying (i.e. the negative slope of the moisture content–time graph) increase relatively rapidly until both reach a constant value. No attempt was made to keep the power input constant by adjusting the controls during the warming-up stage, and the power absorption was found to increase slightly in every case. The reason for this is that the capacity of the system remains almost constant, since very little water is evaporated in the first stage, but the loss factor of the material goes up because the power factor increases with increasing temperature. In the figures where the power is not shown to increase during this stage, the reason is that the run was started with the sample hot.

CONSTANT-RATE PERIOD

In the next stage water is evaporated at a constant rate. and the power input to the oscillator kept constant by continual retuning of the Lecher wire system, which is made necessary by the decrease in the capacity of the system as a whole due to loss of water. In Fig. 13 the power input was decreased after ten minutes while still in the constant-rate period, and in consequence the moisture content–time curve changes in gradient at this point though still remaining linear. This shows that the rate of drying depends only on the power input and is otherwise constant during this period. The temperature reached in this stage is a function of the size and shape of the sample as well as the power input, and though not altering much in this rate period, the constancy of the value depends on the material. When drying wool felt (Fig. 5) the temperature reached 100°c. because of the pack density of the specimen, which reduced heat losses from the surface. The temperature was only 75°c. when the wool was in the less compact form of knitted fabric (Fig. 3).

DECREASING-RATE PERIOD

The moisture content at which this last phase starts will be referred to as the *break point*, and is recognised by a sharp decrease in the cathode current of the oscillator (i.e. a sudden fall in the power input) which can no longer be compensated for by tuning. Simultaneously the rate of drying, constant up to this point, decreases progressively until the material is completely dry. The power input also falls progressively from this point, but does not reach zero when the material is dry, and the final value depends on the loss factor of the material itself. The break points of all the different materials examined are listed in Table I.

The temperature of the sample invariably changes at the break point. In the case of wool and the regenerated protein fibres it falls and soon reaches a constant value, whereas with silk the temperature rises to a steady value at 120°c. The temperature of all the cellulosic fibres, with the exception of Tenasco, increases as dryness is approached, but otherwise they differ greatly amongst themselves and no generalised picture can be presented. It is not clear why viscose rayon should heat up so much more than cotton and

Change of Moisture Content, Power Consumption, and Temperature with Time
(FIG. 3–8)

M —×— Moisture content, g./100 g. of dry textile
P —△— Power consumption, watts
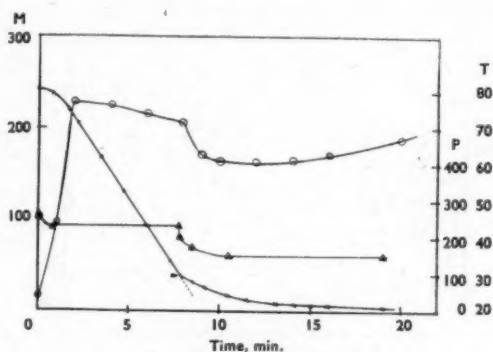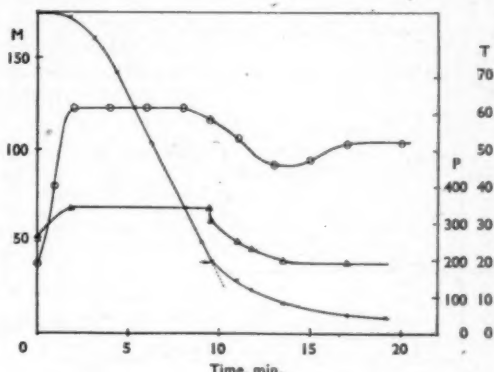T —⊕— Temperature, °C.
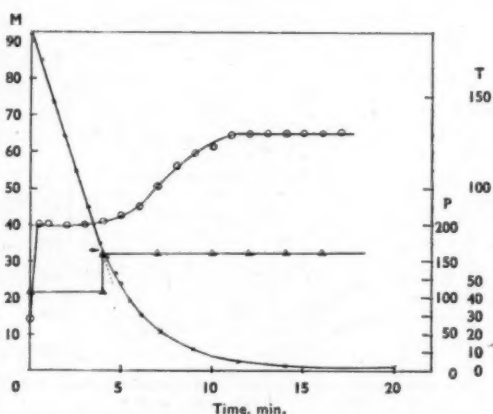→ Break point

FIG. 3— Wool (Knitted Fabric)
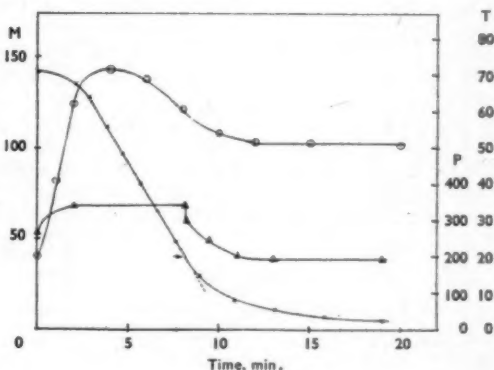

FIG. 6— Ardil

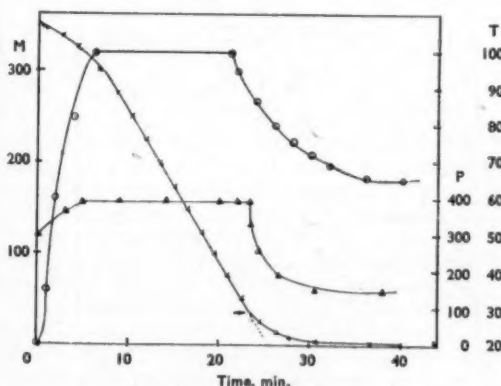
FIG. 4— Wool (Knitted Fabric)
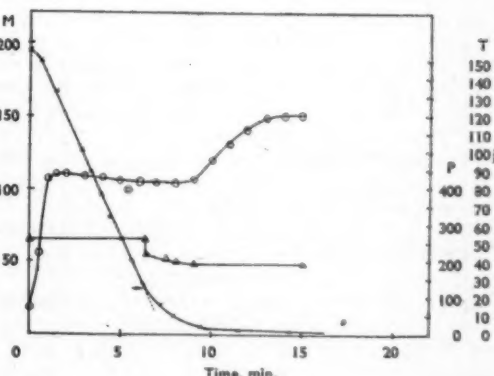

FIG. 7— Aralac

FIG. 5— Wool (Matted Felt)

FIG. 8— Silk

Change of Moisture Content, Power Consumption, and Temperature with Time
(FIG. 9–14)

M —×— Moisture content, g./100 g. of dry textile
P —△— Power consumption, watts
T —⊙— Temperature, °C.
—→ Break point

FIG. 9— Cotton

FIG. 12— Fortisan

FIG. 10— Viscose Rayon

FIG. 13— Tenasco

FIG. 11— Cuprammonium Rayon

FIG. 14— Nylon

Change of Moisture Content, Power Consumption, and Temperature with Time

(FIG. 15–17)

M —×— Moisture content, g./100 g. of dry textile
P —△— Power consumption, watts
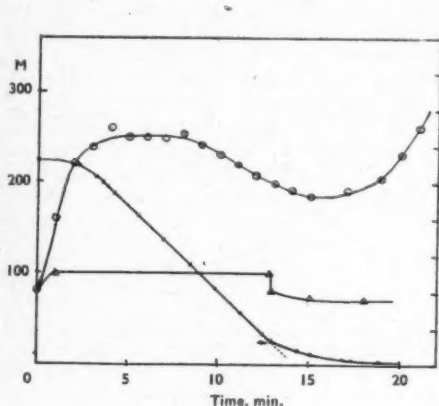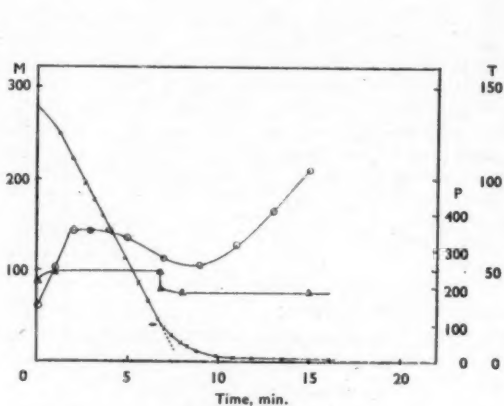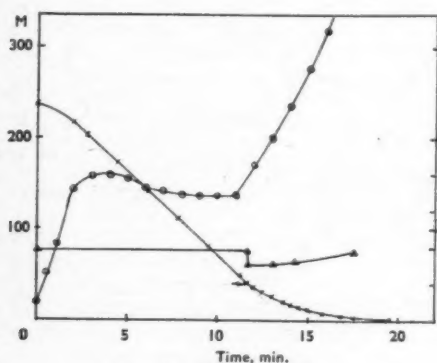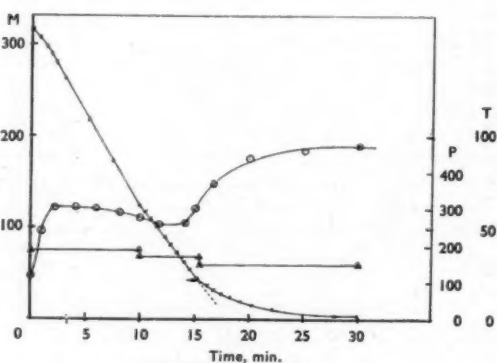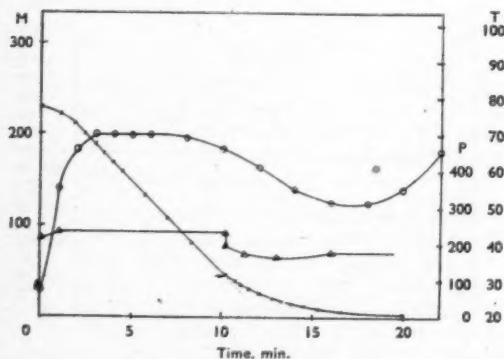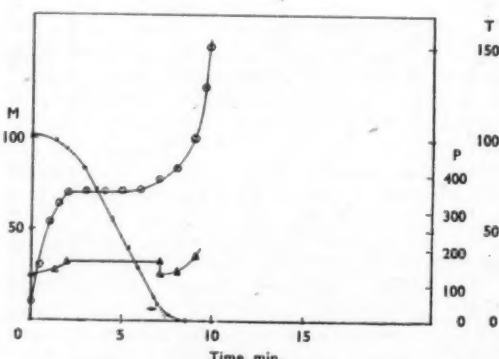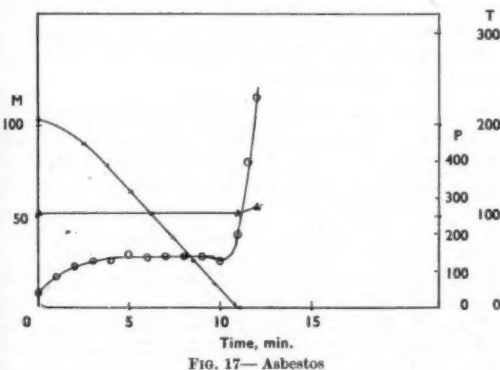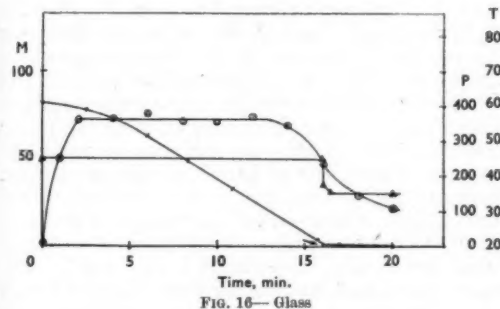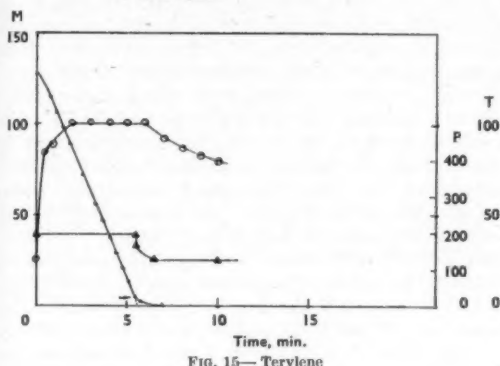T —⊙— Temperature, °C.
→ Break point

FIG. 15— Terylene

FIG. 16— Glass

FIG. 17— Asbestos

cuprammonium rayon. The variations between Tenasco and ordinary viscose rayon are particularly interesting, since they differ only in the degree of orientation of the molecules. In general, the temperature of the samples during this last stage of drying depends largely on the equilibrium temperature of the dry sample, which is a function both of the heat losses of the specimen by convection and radiation and of the electric loss factor of the material itself. In the case of materials which have a high loss factor (i.e. high power absorption) even when dry, the final temperature may be very high

(e.g. an asbestos sheet will attain red heat, and in the case of nylon the melting point of the material is reached). All other textile materials, however, have a relatively low loss factor, so that they cannot easily be overheated, and in the case of glass fabric the equilibrium temperature was only 10°c. higher than that of the room. In every case, however, the power factor of water is many times greater than that of the textile material, so that the wet parts of a non-uniformly moist specimen will always take up power preferentially.

TABLE I

"Break Points" of Textile Materials

(% water content)

Wool	...	...	...	...	...	35
Wool (felt)	...	...	...	...	...	35
Ardil (regenerated protein fibre)				...		38
Aralac (regenerated protein fibre)				...		40
Silk	...	...	...	...	...	30
Cotton	...	...	...	...	...	28
Viscose rayon	...	...	...	...	...	40
Cuprammonium rayon	...	...	...	...	45
Fortisan (high-tenacity rayon)	...		...		40
Tenasco (high-tenacity rayon)	...		...		38
Nylon	...	...	...	...	...	7
Terylene	...	...	...	...	...	4
Glass	...	...	...	...	...	2
Asbestos	...	...	...	...	...	0

In the experiment shown in Fig. 4, the conditions of drying were arranged, by retuning the circuit, to have a low power input during the constant-rate stage and to have a high voltage gradient when the material becomes dry and its capacity becomes small. In this way it was possible to increase the power input at the break point instead of, as in all the other experiments, allowing it to fall. It is important that, in spite of the increased power input as the material dried and the corresponding great increase in temperature of the sample (cf. Fig. 3 and 4), the rate of moisture loss decreased at the same point.

Discussion

KINETICS OF DRYING

The first detailed and experimentally reliable work on textile drying was carried out by Fisher[6] in 1923, who studied the rate of evaporation of water from wool samples suspended over a sulphuric acid desiccant. He found that, if drying rate was plotted against moisture content, a curve showing three distinct regions was obtained. These regions are (1) a constant-rate drying region down to about 30% moisture content; (2) a falling-rate region, in which the rate of drying is a linear function of moisture content; and (3) the final region, from about 10% moisture content to dryness, where the curves bend in a complex fashion towards the origin. Fisher explained these results by postulating pores in the wool fibres, and considered that the constant-rate period was the drying up of the mechanically held water; that the decreasing-rate period was due to the drying up of pores with resultant decrease in drying area; and that the third period corresponded to the removal of "bound" or chemisorbed water. Sherwood[7] in 1929 observed the drying rates of wood, wood pulp, and allied materials, and reached similar conclusions to Fisher. Cowen[8], in a review of the drying process in 1939, designated the value of moisture content at

which the constant-rate region changed to the falling-rate region the "critical moisture content", which he believed to be equivalent to the regain at 100% relative humidity. Preston and Chen[9], in a recent study of the mechanism of the drying of textiles heated by radiation from infra-red lamps, found that, when the temperature of the fabric was plotted against time, a curve was obtained showing three regions corresponding to the three regions in the rate-of-drying curve. They defined the critical moisture content as the moisture content at which the temperature of the sample first began to rise, this corresponding to the value at which the drying rate first began to fall. Wilhelm and Paul[10] also examined infra-red drying in the same way, but their experimental conditions differed in that their samples were freely exposed to convection of cold air, while the samples in Preston and Chen's work were contained in a small oven. Wilhelm and Paul found that the drying rate for wool decreased slowly as the moisture content fell from 200% to 30%, but at the latter value a sharp change in drying rate occurred.

It is evident that in the region of the saturation moisture content of textiles a sharp change takes place in their properties. Table II compares (1) the saturation regain (values are given at about room temperature, though it varies to some extent with temperature), (2) the critical moisture content as determined by Preston and Chen, (3) the water firmly bound by textile fibres as determined by volume changes at the freezing point[11], and (4) the "break point" on the dielectric drying curves.

TABLE II

Material	Moisture Uptake (%)	Relative Humidity (%)	Moisture Content (%) at— Critical Point[9]	Break Point	Bound Water (%)
Cotton ...	22·6[12]	100	26	28	4·3-12[11]
	17·5[13]	100			
	23·0[18]	100			
Wool ...	26-29[14]	95	39	35	5[8]
	34[15]	100			
	32[16]	100			
	35[14]	100			
Silk ...	24[14]	95	27	30	—
	33[14]	100			
Nylon ...	8-10[14]	95	—	7	8·0[11]
Rayon ...	33-46[17]	100	38	40	19[11]

SIGNIFICANCE OF THE "BREAK POINT"

The moisture content at the break point determined by R.F. drying is a well defined quantity at which the dielectric properties of the material change suddenly, shown by the sudden drop in power input to the sample. It cannot simply be due to the oscillator reaching its maximum voltage at the particular capacity of the specimen to be dried, since this would give a break at a given water content independent of the material used. Moreover, a break in the drying rate occurs even when the power input does not fall (Fig. 4). It will be seen from Table II not only that the moisture content at the break point varies from material to material, but also that the value is very similar to the saturation regain and also to the critical moisture contents obtained by Preston and Chen.

At the break point, the loss factor decreases suddenly, which suggests that the water content

below this point must be bound in some way with an energy greater than the water–water hydrogen bond, but not so firmly as to lead to different freezing points. If the water were merely held mechanically in pores, it would not have different high-frequency electric properties from those of free water. However, the pore theory has been disproved in the case of wool by Mellon, Korn, and Hoover[19], who obtained the same adsorption data from powdered wool reprecipitated from thioglycollate solution as had been obtained from the fibrous material. If the water were held in solid solution, as suggested by Hailwood and Horrabin[20], it would also be unlikely to have different electrical properties, and the break point would not occur at the saturation regain. However, Bull[14] and Cassie[21] have shown that the Brunauer, Emmett, and Teller[22] multilayer theory can be adapted to explain the mechanism of adsorption of water by textiles, and since the heat of adsorption for the formation of the final multilayers is about 2·3 kg. cal. per mole[21], this water would be expected to have a different power factor from that of free water. Fricke and Parker[23] have shown that the dielectric properties of gelatin–water gels show very anomalous behaviour, the loss factor rising to a maximum value several times greater than that of free water when the pressure of water vapour above the gel equals that of pure water, i.e. at saturation regain. From these considerations it would be expected that a sharp change would occur in the dielectric properties of a textile material at the 100% R.H. regain value, and since the break moisture content values agree substantially with those previously published for the 100% R.H. moisture content, we consider that this method may give more accurate values for the moisture content at 100% R.H. than have hitherto been obtained by more direct methods, which are always open to criticism because of the possibility of actual condensation taking place.

PRACTICAL ADVANTAGES OF DIELECTRIC DRYING

Dielectric drying possesses considerable advantages over all other forms of drying. Heat is generated in the body of the material to be dried, and in consequence no transfer mechanism is involved, and no heat storage is necessary. However rapidly water is evaporated, overheating during the drying process cannot occur, unless the loss factor of the dry material is greater than that of water. If, as is usually the case, the wet material has a very much higher loss factor than the dry, heat is developed only in the wet parts, ensuring perfectly even drying. It will be seen from the results obtained that wool is eminently suitable for the process, as the temperature of the material falls as it dries. It is possible to overheat wool by the choice of unsuitable conditions (Fig. 4), but once a machine has been correctly set it is impossible to damage wool goods by incorrect process timing. Cotton and regenerated celluloses have a higher dry loss factor than wool, and in consequence the temperature tends to rise as complete dryness is approached, but the rise is not as a rule such as to damage the goods by overheating. Nylon would be relatively easily damaged by overexposure, but

Terylene has a very low loss factor when dry and, like glass, is practically impossible to damage by overheating under the conditions which would obtain in a dielectric drier. The fact that a material overheats when dry does not necessarily render it unsuitable for the process; it merely removes the advantage of self-compensation. Even asbestos and the polyvinyl chloride fibre Vinyon, which have very high dry power factors, can be dried without overheating, although the temperature of these materials rises very rapidly as dryness approaches, causing the Vinyon fabric to melt. The size, shape, and surface area of the piece to be dried are not nearly as important in R.F. drying as in other methods, since the rate of heat generation is a function of the volume of the piece and does not depend on the surface area exposed. In fact, R.F. heating is the only method of quickly heating a thick batch of material, such as a roll of fabric, without scorching the outside. Moreover, owing to the absence of any temperature gradient, there will be no tendency for water movement through the fabric and no danger of dye migration during drying[24]. The twist setting of rayon on cones can be carried out in less than a minute by heating the wet material evenly throughout to 100°c. with R.F., and this process has already found wide application in the United States of America[25].

Since heat is generated only when and where required, the efficiency of conversion of power drawn from the mains into water evaporated is high. In the small generator used in these experiments, about 600 w. was drawn from the mains to give an R.F. output of 250 w., resulting in an overall efficiency of about 40%. About 150 w. is drawn on standby, mainly consumed by the valve cathodes, so that the actual efficiency of conversion of the high-tension power supplied to the valves is nearer 55%. The heat output was some 850 B.Th.U. per hour on full load, representing a rate of evaporation of $1\frac{1}{4}$ lb. of water per hour. A generator of commercial size to evaporate 100 lb. of water per hour would consume approx. 60 kw. from the mains, and the equipment would cost some £3000. The oscillator valves have a limited life of about 5000 hr. and cost £50 or more each to replace. Assuming amortisation over 5 years, and including valve replacements and power at $\frac{1}{2}$d. per kilowatt-hour (kWh.) but excluding labour charges, water would cost 1d. per pound to evaporate. The Radio Corporation of America give the running costs per kWh. as 3·5 cents including maintenance and replacement, based on an actual power cost of 1 cent per kWh.

The cost of drying is therefore approximately six to ten times greater with R.F. than in an efficient steam drying system. However, for some applications the increased speed and the possibility of handling materials in compact masses (e.g. rolls of fabric) may so reduce labour costs as to make the process economic. The improved quality due to the evenness of the heating and the impossibility of heat damage may also, in many cases, outweigh the increased cost.

The curing of resins or the fixation of dyes padded on in a continuous process appear to lend themselves to R.F. heating, because of the more even distribution which is certain to result as there is no moisture content gradient.

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The Reaction of Wool with Organic Chloroamines
I—Conditions for rendering Wool Non-felting

P. Alexander, D. Carter, and C. Earland

It is shown that certain chloroamines will react with wool to render it unshrinkable, but only in the presence of high concentrations of hydrogen and chloride ions. In the absence of high concentrations of these ions the chloroamines still react with the wool, which does not, however, become unshrinkable unless very high concentrations are employed.

From a practical point of view the use of chlorosulphamic acid is most promising in the presence of high concentrations of sodium chloride, as small quantities of available chlorine then render the wool completely unshrinkable with a minimum of damage.

Introduction

Wool may be rendered non-felting either by modifying the surface structure or by changing the elastic properties of the fibres[1,2]. The former may be brought about by degrading the surface with chemical reagents or with abrasives, or by the surface deposition of polymers; while the latter may be achieved by depositing a resin within the fibres or by the use of metallic salts which act as cross-linking agents. Although surface degradation by chemical reagents is the oldest method of making wool fabric unshrinkable, it is still the only method used extensively in practice, for, although it suffers from some disadvantages such as loss in weight of the finished material, the high cost and difficulty of application of the newer methods have prevented their large-scale use. Chemical reagents which render wool non-felting range from oxidising agents such as fluorine[3], potassium permanganate[4,5], and ozone[6] to reducing agents such as thiols[7] or even to alkalis[8], but nearly all commercial methods make use of chlorine in aqueous solution. According to the pH of the solution, the chlorine may be present as such, as hypochlorous acid, or as the hypochlorite ion. Gaseous chlorine has been successfully used[9], but, although chlorine dissolved in an organic solvent is effective[10], the inherent technical difficulties of a solvent process have prevented its widespread application.

The advantages of the aqueous acid chlorine process— low cost and the production of a high degree of unshrinkability— are offset by its rapidity of action, which causes local overtreatment if working conditions are not rigorously controlled. In order to reduce the speed of reaction, nitrogen compounds have been added to the chlorinating bath (e.g. glycine[11], amides, or urethanes[12]), which under the acid conditions employed produced the corresponding chloroamine—

$$R \cdot NH_2 + Cl_2 \rightleftharpoons R \cdot NHCl + HCl$$
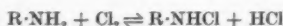
Chloramine - T (sodium N - chloro - p - toluene - sulphonamide)[13], NN-dichloroacetamide, N-chlorophthalimide[14], and N-chlorosulphamic acid[15] have been used to render wool unshrinkable, while the use of chloroamines in conjunction with permanganate has also been described[16]. Although it has been recognised that these compounds may be used to render wool non-felting, no detailed study has been made of their reactions with wool. It has been assumed that chloroamines react with wool via free chlorine or hypochlorous acid, depending on the pH of the solution—

$$R \cdot NHCl + H_2O \rightleftharpoons R \cdot NH_2 + HOCl$$
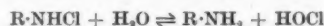
In view of the fact that preliminary experiments cast serious doubts on the validity of this assumption, a detailed survey has been made of the reaction between a number of chloroamines and wool, especially with regard to the mechanism of the reaction and the properties of the finished material. A more detailed study was also made of the effect, discovered by Earland, Bailey, and Carter[17], that the addition of chlorides to the chloroamine solution greatly promotes the resistance to shrinkage of fabric.

Experimental

1. MATERIALS

The wool used was a two-fold 18s yarn of 56/58s quality knitted into fabric using 12 needles and 18 courses per inch and cut into 5-in. or 7-in. single or double squares. These pieces had a dry weight of approx. 5 g., 10 g., 10 g., and 20 g. respectively. Before use all patterns were scoured in dilute soap and ammonia and then thoroughly washed in water.

With the exception of the commercially available chloramine-T, all chloroamines were synthesised by means of one of the two following standard methods—

$$R \cdot NH_2 + HOCl = R \cdot NHCl + H_2O \qquad (i)$$
$$R \cdot NH_2 + Cl_2 = R \cdot NHCl + HCl \qquad (ii)$$
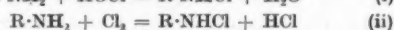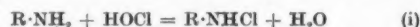
The chloroamines used in this investigation are shown in Table I. They were analysed for available chlorine by treatment of a known weight with potassium iodide and acetic acid followed by titration of the liberated iodine with 0·10 N. sodium

TABLE I

| Compound	Formula	Available Chlorine (%) Found	Available Chlorine (%) Theory	Method of Preparation
N-Chloroethylamine ...	$C_2H_5 \cdot NHCl$	*	89·3	(i)
N-Chlorodiethylamine ...	$(C_2H_5)_2NCl$	64·6	66·0	(i)
N-Chlorourea ...	$NH_2 \cdot CO \cdot NHCl$	*	75·1	(ii)[18]
N-Chloroacetamide ...	$CH_3 \cdot CO \cdot NHCl$	71·5	75·9	(ii)[19]
NN'-Dichlorobiuret ...	$NH(CO \cdot NHCl)_2$	75·8	82·6	(ii)[20]
N-Chlorourethane ...	$NHCl \cdot COOC_2H_5$	46·4	57·5	(ii)[20]
N-Chlorosuccinimide ...	$\begin{matrix} CH_2 \!-\! CO \\ \quad\quad\quad NCl \\ CH_2 \!-\! CO \end{matrix}$	52·4	53·2	(i)[21]
Toluene-p-sulphonsodio-chloroamide ... (chloramine-T)	$p\text{-}CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NNaCl,3H_2O$	24·5	25·2	Laboratory reagent
N-Chlorosulphamic acid	$NHCl \cdot SO_3H$	*	46·2	(i)

* Not isolated from aqueous solution

thiosulphate solution. Where isolation from solution proved difficult, a known volume of the solution was analysed.

Other chemicals used were Analar reagents with the exception of sodium chloride, which was of B.P. quality. It was essential that all chlorides were free from bromides, as active chlorine compounds oxidise the latter to free bromine, which would have vitiated the results. B.P. Sodium chloride was quite satisfactory, as it gave a negative test for bromide, and duplicate experiments performed using sodium chloride of Analar and B.P. quality were identical.

2. APPLICATION TO WOOL

Since each atom of chlorine in a chloroamine liberates two atoms of iodine from acidified potassium iodide—

$$R \cdot NHCl + 2KI + CH_3 \cdot COOH$$
$$= R \cdot NH_2 + CH_3 \cdot COOK + KCl + I_2$$
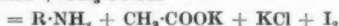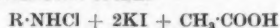
and all calculations have been based on the relationship—

1 litre $N-Na_2S_2O_3$ solution $\equiv 35 \cdot 5$ g. chlorine

the quantities of oxidising agents are expressed in terms of "active" or available chlorine. The actual number of chlorine atoms corresponds to half this value. The percentages of oxidising agents given are based on the weight of wool containing 14% water.

The fabric was wetted out in 1% aqueous Dispersol VL (ICI), washed off, and squeezed. It was then sewn on to a glass stirrer driven at 100 r.p.m., and entered into an aqueous solution of the chloroamine. After the bath had exhausted, the patterns were washed in cold water and then neutralised in dilute ammonia (1 ml. of 0·880 ammonia soln. per 100 ml. of water).

Unless stated otherwise, the wool was treated with the chloroamine, equivalent to 4·0% available chlorine, calculated on the weight of fabric, in 0·50% sulphuric acid solution at 40°c. using a liquor : wool ratio of 80 : 1. Where the reaction was performed in the presence of chloride, sodium chloride was added to give a 10·0% solution. Before the wool was entered, a 5-ml. portion of the bath was titrated iodometrically using 0·10 N. sodium thiosulphate solution delivered from a microburette. Throughout the treatment the progress of the reaction was followed by iodometric titrations on aliquot portions of the bath removed at intervals of 5 or 10 min. The initial titration ensured that the correct amount of oxidising agent was in the solution, and allowed the time for half the active chlorine content of the bath to disappear to be calculated. This value, the half-life $t_{\frac{1}{2}}$, is expressed in minutes, and was reproducible to ± 1 min. Since these reactions are pseudo-unimolecular and the rate is independent of stirring, $t_{\frac{1}{2}}$ can be used as a measure of the rate of reaction of the oxidising agent with the wool. The rate-controlling step is probably diffusion within the fibre[22].

The quantity of wool treated depended on the milling procedure, and varied from a single 5-g. pattern for hand-milling to two 20-g. patterns for the Hotpoint washing machine. In the single-fibre experiments a 1-g. bundle of Lincoln fibres was treated with the calibrated fibre for testing amongst them.

3. SHRINKAGE TESTING

Shrinkage testing was done either by vigorous hand-milling in 1% soap solution at 30°c. or by the use of a Hotpoint washing machine or experimental milling stocks under conditions described previously[5], the area of the pattern being measured before and after the test. At least one untreated control pattern was always tested together with the treated pattern. Before determining the area prior to shrinking, all patterns were allowed to recover from mechanical stress, i.e. to relax, by immersion for at least one hour in a soap solution.

The shrinkage of patterns tested in the washing machine varied with pattern size. It is seen from Table II that this variation was eliminated by using double patterns at least 7 in. square. Consequently, patterns of this size were always used for testing in the Hotpoint washing machine. For felting by hand-milling or in the milling stocks, 5-in. square patterns were satisfactory.

TABLE II
Shrinkage of Untreated Patterns in Washing Machine

Size of Double Square Pattern (in.)	Weight (g.)	Area Shrinkage of Pattern (%) 53 min.	106 min.
12	60	16·0	27·3
7	20	17·2	24·9
5	10	7·5	11·3

4. ALKALI SOLUBILITY

The sample of known dry weight was treated for one hour at 65°c. with 0·10 N. sodium hydroxide at a liquor ratio of 100 : 1[23]. The wool was recovered in a Büchner funnel, washed free from alkali, and dried at 110°c. The alkali solubility is expressed as the percentage loss in weight.

5. WET ABRASION RESISTANCE

The knitted fabric was abraded on a Tootal Broadhurst Lee ring wear tester against a standard woven wool fabric, and the number of revolutions to produce a hole recorded. The specimen was impregnated with a buffer solution at pH 7, and the results were expressed as a percentage of the number of revolutions required to wear an untreated fabric tested at the same time.

6. LATENT DAMAGE TEST

During the course of this investigation it was sometimes found that treated fabric which possessed good wet and dry abrasion resistance was badly damaged after neutral dyeing. To meet this contingency, the following test was devised— The fabric was boiled for 2 hr. in a solution containing 0·50 g. of sodium pyrophosphate per litre at a liquor ratio of 50 : 1. The fabric was rinsed in cold water and impregnated with a pH 7 buffer solution, and the abrasion resistance determined wet as described previously. The results are expressed as a percentage of the value for untreated fabric which had also been boiled in pyrophosphate.

Results

1. IMPORTANCE OF CHLORIDE IONS

Table III shows the shrinkage results obtained on hand-milling patterns treated with different chloroamines, equivalent to 3% available chlorine, in the absence and in the presence of chloride ions.

TABLE III
Effect of Chloride

Compound	Temp. (°c.)	Acid	Acid Concn. (% wt./vol.)	NaCl Concn. (%wt./vol.)	Half-life (min.)	Area Shrinkage (%) Treated	Un-treated
NH₄·CO·NHCl	40	H₂SO₄	0·50	0	57	21·7	22·8
		H₂SO₄	0·50	10·0	10	−2·8	24·0
		HCl	0·092	2·5	32	29·4	26·6
		HCl	0·092	10·0	14	2·6	23·7
CH₃·CO·NHCl	75	CH₃·COOH	5·0	0	∞	—	—
		CH₃·COOH	5·0	10·0	∞	—	—
		H₂SO₄	2·25	0	38	12·0	26·9
		HCl	1·84	0	22	−1·8	17·5
NH(CO·NHCl)₂	60	CH₃·COOH	5·0	0	∞	—	—
		H₂SO₄	2·25	0	30	20·0	25·0
		HCl	1·84	0	5	0·3	23·2
CH₂—CO\ | NCl CH₂—CO/	75	CH₃·COOH	5·0	0	10	22·9	21·1
		CH₃·COOH	5·0	10·0	10	22·3	31·4
		HCl	1·84	0	15	5·1	24·2
p-CH₃·C₆H₄·SO₂·NCl₂*	40	H₂SO₄	0·50	0	8	10·5	24·4
		H₂SO₄	0·50	10·0	4	−3·3	29·5
NHCl·SO₃H	40	H₂SO₄	0·50	0	7	21·4	22·0
		H₂SO₄	0·50	10·0	7	1·6	22·0
NHCl·CO·OC₂H₅	40	H₂SO₄	0·50	0	∞	—	—
		H₂SO₄	0·50	10·0	9	−1·0	24·2

* In acid solution chloramine-T is converted to the dichloro derivative.

These preliminary experiments established the fact that chloroamines reacted in strongly acid solution (below pH 2) with wool keratin. In the presence of chloride ions, i.e. on acidifying with excess of hydrochloric acid or on adding sodium chloride, resistance to milling shrinkage was conferred upon fabric. However, when the solution was acidified with sulphuric acid little or no shrinkage resistance was obtained. Further experiments established that the action of chloride ions was specific: e.g. fluoride, sulphate, and nitrate ions did not produce the effect, while iodide and bromide ions were oxidised immediately to the free halogen. Although sodium chloride was used throughout this investigation, other soluble chlorides were shown to function equally effectively at the same molar concentrations.

The importance of chloride ions is further illustrated in Tables IV, V, and VI. A typical chloroamide, N-chlorourea, and a chlorosulphonamide, chlorosulphamic acid, were selected for a more detailed study.

TABLE IV
Area Shrinkage (%) in Washing Machine after Treatment with N-Chlorourea

Available chlorine	...	...	...	4·0%
Time in washing machine	...	...	106 min.	
Shrinkage of untreated pattern	...	30·4%		

NaCl Concn. (% wt./vol.)		H₂SO₄ Concn. (% wt./vol.)	
	0·45	1·80	3·60
0	15·7	13·8	15·0
1·0	17·2	17·4	8·6
5·0	10·2	6·2	1·1
7·5	7·5	6·8	6·3
10·0	5·3	3·6	4·6

Tables IV and VI show that the acidity and sodium chloride concentration of the chloroamine solution are interrelated. As the acidity of the solution is increased, a lower concentration of sodium chloride is necessary for the solution to render wool non-felting. The practical importance of the

TABLE V
Area Shrinkage (%) in Washing Machine after Treatment with N-Chlorourea in 0·50% Sulphuric Acid

	Shrinkage of untreated pattern	...	18·1%	
NaCl Concn. (% wt./vol.)	N-Chlorourea (% available Cl₂ on wt. of wool)			
	3·0	4·0	6·0	8·0
0 ...	19·2	13·1	4·5	6·3
3·0 ...	12·9	11·0	3·0	4·5
5·0 ...	11·8	10·2	2·8	0·9
10·0 ...	4·0	2·6	2·6	1·7

TABLE VI
Area Shrinkage (%) on Hand-milling after Treatment with Chlorosulphamic Acid

Available chlorine	...	...	...	4·0%
Shrinkage of untreated pattern	...	22·0%		

NaCl Concn. (% wt./vol.)		H₂SO₄ Concn. (% wt./vol.)	
	0·10	0·20	0·50
0 ...	23·4	20·4	21·4
2 ...	15·1	13·6	8·8
4 ...	14·4	14·5	2·0
6 ...	12·4	5·3	5·5
8 ...	3·7	1·4	−6·3
10 ...	5·7	−0·2	1·6

chloride effect is that it enables these substances to be used in solutions of lower acidity than if chloride were absent, thus decreasing the tendency for the wool to be damaged by acid.

From Table V it is seen that in the presence of a sufficient concentration of chloride the quantity of chloroamine required to render wool unshrinkable is only half that necessary when the solution is free from chloride.

Although in solution below pH 2 reaction between wool keratin and chloroamines occurred whether chloride ions were absent or present, in the case of N-chlorourea the addition of chloride increased the rate of the reaction (Table VII).

TABLE VII
Variation of Half-life of N-Chlorourea in 0·092% HCl with Chloride Concentration

NaCl Concn. (% wt./vol.)		Half-life (min.)
2·0	...	35
4·0	...	25·5
6·0	...	21·5
8·0	...	17
10·0	...	15
12·0	...	13
14·0	...	11
16·0	...	11

A possible explanation of the rôle of chloride ions in promoting the production of unshrinkability seemed to be the increase in the rate of the reaction, which would tend to confine the attack to the fibre surface, whereas the slow reaction in the absence of chloride ions would tend to be more extensive. This theory is, however, untenable, since the rate of reaction of chlorosulphamic acid with wool is independent of chloride ion concentration (Table VIII), although no unshrinkability is obtained in the absence of chloride.

TABLE VIII
#### Variation of Half-life of Chlorosulphamic Acid with Chloride Concentration

NaCl Concn. (% wt./vol.)	Half-life (min.)
0*	7
2	6
4	5
6	7
8	7
10*	7

Moreover, the rate is independent of stirring, and the rate-determining process in the reaction between wool and chlorosulphamic acid was not diffusion through a liquid film[22], since treatments marked (*) gave the same half-life times when the wool was also stirred at 400 r.p.m. instead of the usual 100 r.p.m.

2. EFFECTIVENESS OF DIFFERENT CHLOROAMINES AS ANTI-FELTING AGENTS

(a) *Chloroamine*

A 5-g. pattern of wool was treated with 400 ml. of a solution containing 10 g. of ammonium chloride, 20 g. of acetic acid, and 4·0% available chlorine on the weight of wool. This solution contained chloroamine, produced by the following reaction—

$$NH_4Cl + HOCl = NH_2Cl + HCl + H_2O$$
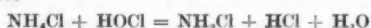
After treatment the pattern, which was very yellow, was hand-milled (Table IX).

TABLE IX
Treatment with Chloroamine

Temperature of Treatment (°C.)	Half-life of Reaction (min.)	Area Shrinkage (%) Treated	Untreated
75	2	22·2	26·2
25	23	27·3	26·2

These treatments were performed at a higher pH than the treatments with organic chloroamines, since chloroamine is unstable in solutions of low pH, in which it is converted to dichloroamine and nitrogen trichloride.

(b) *Alkylchloroamines*

The shrinkage of fabric treated with N-chloroethylamine and N-chlorodiethylamine is shown in Table X.

TABLE X
Shrinkage in Washing Machine after Treatment with N-Chloroethylamine and N-Chlorodiethylamine

Shrinkage of untreated pattern ... 25·7%

Chloroamine	NaCl Concn. (% wt./vol.)	Area Shrinkage (%)
$C_2H_5 \cdot NHCl$	0	26·3
	10·0	9·2
$(C_2H_5)_2NCl$	0	31·1
	10·0	11·5

(c) *Chloroamides*

Although it has been shown (Table IV) that fabric treated with N-chlorourea under certain conditions was completely resistant to washing in soap solution, fabric treated similarly felted badly when milled in the stocks with soap (Table XI) or when washed in acid (Table XII)[5].

TABLE XI
Milling of Fabric treated with N-Chlorourea

Method of Felting	Time of Felting (min.)	Area Shrinkage (%) Treated	Untreated
Milling stocks ...	30	6·5	17·3
	60	16·7	33·4
Washing machine	53	− 6·3	19·9
	106	− 8·3	30·0

TABLE XII
Acid Washing of Fabric treated with N-Chlorourea

Method of Felting	Time of Washing (min.)	Area Shrinkage (%) Treated	Untreated
0·50 N. Acetic acid ...	53	18·0	28·6
	106	29·3	40·6
0·50% Sodium oleate ...	53	− 6·3	19·9
	106	− 8·3	30·0

(d) *Chlorosulphonamides*

Table XIII shows that fabric treated with chlorosulphamic acid (in the presence of sodium chloride) completely resisted milling in the milling stocks.

TABLE XIII
Milling of Fabric treated with Chlorosulphamic Acid

Pattern	Time of Felting (min.)	Area Shrinkage of Pattern (%)
Treated	30	1·2
		0
	69	3·7
		3·8
Untreated	30	30·8
		33·6
	60	39·5
		46·7

It has been shown that N-chlorourea is far less effective in promoting resistance to felting than chlorosulphamic acid, for fabric treated with the former in the presence of chloride is resistant to washing only. To determine if, in general, fabric treated with chlorosulphonamides resisted felting in the mill while treatment with chloroamides produced material resistant to washing only, fabric was treated with NN'-dichlorobiuret and chlor-amine-T in the presence of sodium chloride and milled in the stocks for 60 min. (Table XIV).

TABLE XIV
Milling of Fabric treated with Chloroamides and Chlorosulphonamides

Compound	Class	Area Shrinkage (%)
Untreated	—	33·2
$NH_2 \cdot CO \cdot NHCl$	Chloroamide	24·3
$NH(CO \cdot NHCl)_2$	Chloroamide	30·1
$NHCl \cdot SO_3H$	Chlorosulphonamide	2·8
$p\text{-}CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NNaCl$ ...	Chlorosulphonamide	3·1

There appears to be a relationship between the structure of the chloroamine and its effectiveness as an anti-felting agent. Alkylchloroamines produce only limited resistance to washing shrinkage; fabric treated with chloroamides completely resists washing, but felts on milling; while treatment with chlorosulphonamides produces fabric which resists milling.

Although it has been shown that fabric treated with chlorosulphamic acid in the presence of sodium chloride resists milling for one hour, it is known that many other treatments, e.g. with acid chlorine, are apparently equally effective. However, it is seen from Table XV that, whereas the shrinkage resistance of fabric treated with acid chlorine breaks down on prolonged milling, this is not the case after treatment with chlorosulphamic acid and the shrinkage resistance is as good as in the solvent processes, which are known to produce permanent unshrinkability.

TABLE XV
Area Shrinkage (%) on Prolonged Milling of Fabric after Different Treatments

Time of milling, hr. ...	0·5	1·0	1·5	2	3	4
Untreated	21·6	48·2	—	—	—	—
4·0% Cl₂ (on wt. of wool) at pH 1·5	4·2	6·2	10·8	26·0	41·7	49·3
8·0% Cl₂ (on wt. of wool) at pH 1·5	4·6	6·4	5·7	10·6	13·0	21·4
Cl₂ in CCl₄[10]	4·5	− 4·6	4·3	3·5	− 1·8	2·3
SO₂Cl₂ in CCl₄[24]	1·3	− 0·6	− 0·4	5·3	3·0	− 1·5
NHCl·SO₃H (≡ 4·0% Cl₂) in presence of NaCl ...	2·0	0	0	1·1	1·1	1·3

Another advantage of the chlorosulphamic process is that it requires no clearing with an antichlor

such as sodium bisulphite. Wool after treatment with aqueous chlorine solutions retains active chlorine even after prolonged washing[25]. It is not known whether the chlorine is retained by physical forces or as a chloroamine, but it is normally removed with sodium bisulphite solution. Fabric after treatment with chlorosulphamic acid possesses no residual oxidising power, as may be shown by treatment with acidified potassium iodide solution, and merely requires washing free from salt and acid with dilute ammonia solution.

3. MECHANICAL PROPERTIES OF CHLOROAMINE-TREATED FIBRES

Scaliness or differential friction effect (D.F.E.) was determined by the violin bow method of Speakman[26] and by the method of Lipson and Howard[27], which produced results in good agreement. No appreciable reduction in the D.F.E. was obtained with chlorosulphamic acid by itself; on addition of salt the effect was almost entirely removed. The effect of salt is much less marked with N-chlorourea, and the D.F.E. is only reduced by about 50%.

TABLE XVI

D.F.E. of Fibres treated with N-Chlorourea and Chlorosulphamic Acid

$$\text{D.F.E.} = \frac{\tan \theta_1 - \tan \theta_2}{\tan \theta_1} \times 100 \quad \text{or} \quad \frac{\mu_1 - \mu_2}{\mu_1 + \mu_2}$$

			Speakman's Method			Lipson and Howard's Method		
Chloroamine	Equivalent Available Chlorine (%)	NaCl Concn. (% wt./vol.)	Angle with Scales, tan θ_1	Angle against Scales, tan θ	D.F.E. (%)	Anti-scale Coefficient μ_1	With-scale Coefficient μ_2	D.F.E.
None	—	—	0·477	0·670	40·2	0·47	0·21	0·38
NHCl·SO₃H ...	4·0	0	0·477	0·642	34·6	0·40	0·26	0·21
		10	0·573	0·608	6·1	0·51	0·41	0·11
NH₂·CO·NHCl	3·0	2·5	0·582	0·716	23·0	0·52	0·37	0·19
		10	0·596	0·703	18·0	0·40	0·30	0·15

The elastic properties were investigated using a modification of an apparatus originally devised by Speakman[28]. The reduction in work to stretch treated and untreated Lincoln fibres 30% is shown in Tables XVII and XVIII. An untreated fibre stretched twice under these conditions showed a reduction in work of 2%.

TABLE XVII

Elasticity of Fibres treated with N-Chlorourea

Available chlorine · ... 3·0%

Acid Concn. (% wt./vol.)	NaCl Concn. (% wt./vol.)	Temp. (°C.)	Half-life of Reaction (min.)	Reduction in Work (%) to stretch 30%
0·092 HCl	2·5	40	32·5	21·9
0·092 HCl	7·5	40	18·0	23·1
0·092 HCl	10·0	50	10·0	22·4
0·60 H₂SO₄	5·0	40	6·0	21·0
1·50 H₂SO₄	10·0	40	6·0	18·9

Although the half-life of the reaction was varied from 32·5 to 6 min., the reduction in work on stretching the treated fibres 30% changed very little. It therefore seems unlikely that more of the reaction is confined to the fibre surface when the rate of reaction is increased.

TABLE XVIII

Elasticity of Fibres treated with Chlorosulphamic Acid

Reagent	Equivalent Available Chlorine (%)	NaCl Concn. (% wt./vol.)	Reduction in Work (%) to stretch 30%
NHCl·SO₃H ...	4	0	14·1
NHCl·SO₃H ...	4	10	10·9
NHCl·SO₃H ...	3	0	7·1
3·0% Cl₂ (pH 1·5)	3	10	12·5

4. PROPERTIES OF FABRIC TREATED WITH N-CHLOROUREA AND CHLOROSULPHAMIC ACID

(a) Microscopic Examination

Wool treated with chlorourea in either the absence or the presence of chloride ions or with chlorosulphamic acid in the absence of chloride ions had an undisturbed scale structure, and the scales were not detached during milling. Treatment with chlorosulphamic acid in the presence of chloride, however, caused considerable surface degradation, and after milling in pH 9 buffered solution a degraded protein layer could be seen on the fibre surface[2].

(b) Alkali Solubility

The alkali solubility of wool treated with N-chlorourea equivalent to 3·0% available chlorine in solution of pH 1·2, with varying chloride concentration, is shown in Table XIX.

TABLE XIX

Alkali Solubility of Wool treated with N-Chlorourea

NaCl Concn. (% wt./vol.)	Area Shrinkage in Washing Machine (%)	Alkali Solubility (%)
Untreated	17·8	10·0
2·0	13·6	14·6
4·0	9·6	14·4
6·0	9·6	18·3
8·0	5·9	21·2
10·0	3·3	19·7
12·0	0·8	19·2
18·0	1·4	22·3

The alkali solubility of wool treated with chlorosulphamic acid, equivalent to 3·0% available chlorine, in the absence of chloride and with 10·0% sodium chloride in the solution, was also determined. In Table XX these values are given, and for comparison the figures after reaction with the same quantity of chlorine at pH 1·5 and pH 9·0.

TABLE XX

Alkali Solubility of Wool treated with Chlorosulphamic Acid

Available chlorine ... 3% on wt. of wool

Treatment	Alkali Solubility (%)
None	9·8
NHCl·SO₃H, no NaCl	20·8
NHCl·SO₃H, 10·0% NaCl soln. ...	20·9
Chlorine at pH 1·5	20·3
Chlorine at pH 9·0	17·5

(c) Wet Abrasion Resistance

The wet abrasion resistance of fabric treated with 3·0% chlorine as N-chlorourea and chlorosulphamic acid is—

Chlorourea	70·5%
Chlorosulphamic acid	75·5%

(d) Latent Damage Test

The results of the latent damage test of treated fabric are shown in Table XXI—

TABLE XXI

Latent Damage Test on Treated Fabric

Treatment	Latent Damage (%)
3% Chlorourea in 2·0% NaCl soln.	52
3% Chlorourea in 10·0% NaCl soln.	41
3% Chlorosulphamic acid in 10·0% NaCl soln.	91

Discussion

It has been shown that certain chloroamines will react with wool to render it unshrinkable with the same quantity of chlorine as, and possibly less than, is necessary when solutions of hypochlorite of high acidity are employed, but only in the presence of high concentrations of hydrogen and chloride ions. In the absence of high concentrations of these ions the chloroamines still react with the wool, which does not, however, become unshrinkable unless very high concentrations are employed, which cause severe degradation. It is probably this fact which has precluded their use in practice; thus a patent[15] which employs chlorosulphamic acid by itself specifies that formaldehyde must also be used, no doubt so as to minimise the damage which is caused by using the high concentrations of chlorosulphamic acid (e.g. 8% on weight of wool) which this patent specifies.

The necessity for the presence of hydrogen and chloride ions in high concentrations, as well as the differences between different chloroamines, will be discussed in a forthcoming publication.

From a practical point of view, the use of chlorosulphamic acid is most promising in the presence of high concentrations of sodium chloride, as small quantities of available chlorine then render the wool completely unshrinkable with a minimum of damage, which is particularly well demonstrated by the latent damage test (cf. Table XXI). Compared with acid chlorination, the use of the chlorosulphamic acid process described here has a number of advantages. Firstly, it is very slow, and hence leads to very even processing; thus, the half-life of the reaction at 40°c. is of the order of 10 min., whereas that of chlorine even at 0°c. is of the order of 2–3 min.[2]. Moreover, acid chlorination cannot be applied under conditions where the reaction rate is independent of stirring and is always controlled by the diffusion of the chlorine through a liquid film adhering to the wool. This, as has been pointed out in a previous publication[2], is liable to lead to uneven processing. Chlorosulphamic acid reacts very slowly with the fibre, and consequently its rate of reaction becomes independent of stirring with a small amount of agitation; the rate is controlled by diffusion within the fibre, which has been shown to favour uniformity of treatment. It will be noted from Table XV that even very severe treatments with acid chlorine solutions do not produce a wool which is permanently resistant to felting, and this is presumably due to unlevelness of treatment, which cannot be avoided even in the laboratory. Chlorosulphamic acid, however, gives a wool which does not felt, even after four hours in the milling stocks, and behaves in this respect in an identical manner to chlorine in carbon tetrachloride, a method of application which would be expected to be uniform. Alkaline solutions of hypochlorite react slowly with wool[2], and in this respect resemble chlorosulphamic acid, but they do not produce a wool which is resistant to felting in the milling stocks, and also they discolour the wool. Wool treated with chlorosulphamic acid is perfectly white and has a good handle. It appears, therefore, that chlorosulphamic acid is able to give a perfectly unshrinkable wool with a minimum amount of damage, and it can be applied by conventional methods. The actual damage figures, as assessed by alkali solubility, abrasion resistance, reduction in work required to stretch a single fibre, are in every case slightly superior to those obtained when wool has been treated with acid chlorine.

It is interesting that chlorosulphamic acid, which produces complete unshrinkability, gives a wool which loses its scales on milling, whereas chlorourea, which produces a wool which does not felt in the washing machine but shrinks severely in a mill, retains its scale structure unimpaired. These observations support the conclusion[29] that, to obtain a wool which cannot felt under any conditions, the scales have to be completely removed, or so loosened that they come off on gentle agitation, whereas unshrinkability under the action of a washing machine can be obtained without changing the microscopic appearance of the scales.

It is a pleasure to acknowledge the advice given by Miss A. Newton, B.Sc., on all matters relating to the testing of shrinkage, and we are grateful to Messrs. Wolsey Ltd. for permission to publish this paper.

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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Absorption Spectra of the Benzoylaminoanthraquinone Vat Dyes

The Editor

SIR,

In pursuance of a general programme of research on the dyeing of cellulose we have carried out measurements of the absorption spectra of various vat dyes in both the reduced and oxidised states. As a result of this some interesting observations have been made on the benzoylaminoanthraquinone vat dyes. In all cases examined there is a characteristic similarity in the absorption spectra of the reduced dyes, all of which show two distinct absorption bands with maxima in the blue and yellow regions respectively. The curves in the oxidised state possess only one absorption band, and have no general similarity (Fig. 1).
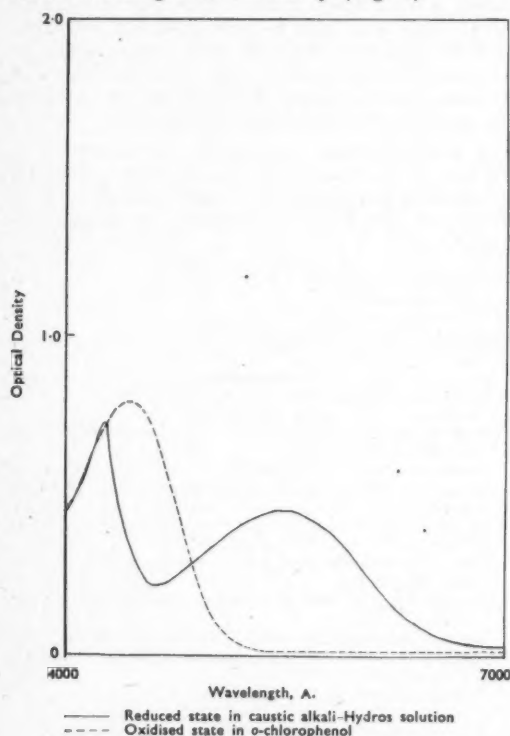

FIG. 1— Oxidised and Reduced Caledon Yellow 3G

— Reduced state in caustic alkali-Hydros solution
---- Oxidised state in o-chlorophenol

In the reduced state the two absorption bands would separately give rise to a yellow and purple colour respectively and, being nearly complementary, are responsible for the dichroic appearance and often indeterminate colour of the vat.

A further interesting observation lies in the fact that, when these dyes are dyed on a highly oriented fibre such as Fortisan and viewed in the reduced state with polarised light, the fibre appears yellow when the plane of polarisation is parallel to the fibre axis and purple when it is at right angles. The chromophoric systems responsible for these two bands in the reduced dye are oriented, therefore, in different directions in the molecule, and quite possibly are at 90° to one another.

In studying the dyes in the oxidised state, absorption measurements were made with a view to determining the extent of aggregation and disorientation of the dye when soaped. Instead of observing a decrease in optical density, as one would expect on aggregation, an increase of up to 100% at the peak wavelength was obtained (Fig. 2).
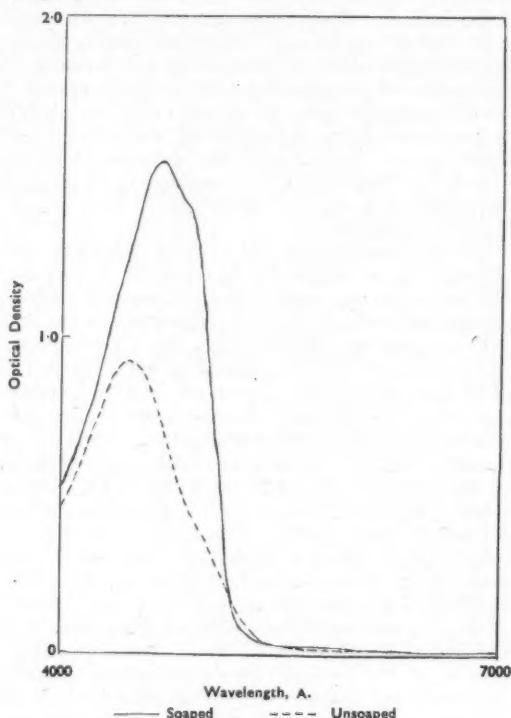

— Soaped ---- Unsoaped

FIG. 2— Oxidised Caledon Yellow 3G on Viscose Film

As this phenomenon, so far as we have observed, is confined to the acylated aminoanthraquinones, an explanation of the effect can be found in the hydrogen-bonding properties of the benzoylamino group. It is probable that these dyes in the pigment form are internally hydrogen-bonded—

Caledon Yellow 3G

(Probable hydrogen-bonded form)
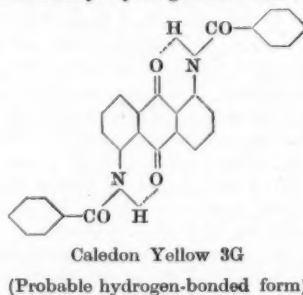
and as internal bonding increases the possibility of resonance, the intensity of colour will be increased. On reduction, however, such bonds will be opened and full development of colour will be dependent on their reformation. It would appear that complete reconversion to the fully bonded pigment form is accomplished only after a vigorous hot soaping (or hot water) treatment. The fact that energy is required to reform the internal hydrogen bond may be due to the activation energy of the normal reconversion process or additionally to the formation during dyeing of a hydrogen bond from the benzoylamino group to the cellulose. Further work on these phenomena is proceeding.

<div align="center">Yours faithfully</div>

<div align="right">E. Waters</div>

Dyehouse Department

    Imperial Chemical Industries Ltd.

        Dyestuffs Division

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                Manchester 9

11th August 1950

Light Flux Integrator

The Editor

Sir,

Since the light flux integrator used by Mr. Seltzer and myself was reported in a paper at the Harrogate Symposium on Photochemistry in relation to Textiles[1], certain modifications have been made to the circuit.

In the earlier instrument an electromagnetic relay was used to operate the message register, which recorded light dosage to the fading pattern. The relay was driven by a double triode valve (type 6F8G), and under the conditions specified an anode current of 20 ma. was drawn from one-half of the valve. This current was sufficient to overheat the valve and reduce its working life.

In addition, the current supply to the message register was drawn from the same high-tension supply as the integrator circuit, and the short current pulses taken by the former were of sufficient magnitude to reduce the H.T. voltage. At high counting rates (3 per sec.), a sensible reduction in H.T. became apparent, its magnitude depending on the counting rate.

In order to make the instrument more versatile and reliable at high intensities, a gas-filled relay V_2 (Osram type GTIC) was substituted for the electromagnetic relay, being provided with a separate supply voltage from a small 80-v. transformer T_2.

The flip-flop circuit remains unchanged, apart from the substitution of a resistance capacity feed (R_3, C_3, R_4) to the thyratron grid.

The small internal switch attached to the message register is used to short the first grid of the flip-flop circuit. An electrolytic condenser is connected in parallel with the counter to prevent chatter during the conduction period of V_2.
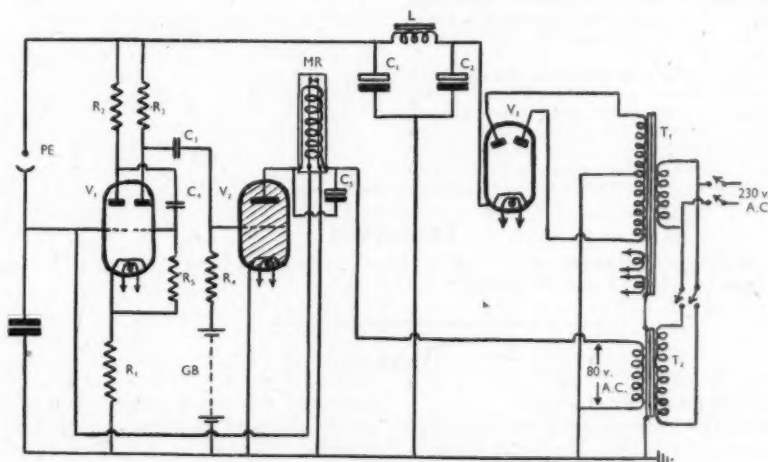
Capacitances
(microfarads)

$C_1 = C_2$	...	16	(350 v. working electrolytic condenser)
$C_3 = C_4$	...	0·1	(350 v. working condenser)
C_5	... ...	8	(350 v. working electrolytic condenser)

Inductance
(henries)

L ... 20 (50 ma. smoothing choke)

Mains Transformers
(volts)

T_1	...	...	300-0-300
T_2	...	...	80

Valves

V_1	...	...	6F8G
V_2	...	...	GTIC
V_3	...	...	5Z4

GB	...	0-v. grid bias battery
MR	...	G.P.O. message register
PE	...	Photocell

Resistances
(ohms)

R_1	...	...	3×10^3
$R_2 = R_3$	...	...	57×10^3
$R_4 = R_5$	...	...	1×10^6

With these modifications, the instrument will measure light intensities on a linear scale for counting rates of up to 5 per second.

<div align="right">Yours faithfully
E. ATHERTON</div>

DYEHOUSE DEPARTMENT
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23rd August 1950

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John Wilson, the First British Dyer of Turkey Red

The Editor

SIR,

With reference to Mr. Hampson's letter of 5th July 1950 (J.S.D.C., **66**, 483 (Sept. 1950)) John Wilson of Ainsworth was undoubtedly the first man in Britain to dye Turkey Red. His own account of his work in this and other fields of dyeing was published by him as *Essay on Light and Colours and what Colouring Matters are that dye Cotton and Linen* (Manchester 1786). A copy of it is in Manchester Central Library. The following quotation is from it—

> The Turkey Red.
> This valuable colour cost me several hundred pounds. In the year 1753, I sent a young man to Turkey, on purpose to learn to dye it. He had lived with Mr. Richard Dobs, a merchant in Smyrna, some time before, and had learned the language of those Greeks who dye it; and by Mr. Dobb's interest, got admittance into their dyehouses, and was instructed; and on his return, brought the true method, and with him many bales of the best madder root, pronounced by them Choke Biaugh, ...
> He executed the business I sent him about, and I rewarded him for his trouble; but when I got it, to my great disappointment it would not suit for my purpose, that is, for cotton velvets; nor in any other sort of piece work I then made. The tediousness of so many operations, and the exactness required, every time rendered it of no more value to me than the madder

root I have herebefore mentioned, which is so easily dyed, whereas the Turkey Red requires 12 or 13 operations in repeated Steepings, Dryings, Washings and Dying.

    However, I will offer my reader a short abstract of the mode of doing it; . . . . . .

The precedence of Ainsworth was admitted by Parnell on p. 10 of his *Dyeing and Calico-Printing* (London 1849), where he also states that the French method of dyeing Turkey Red was introduced into Britain at about the same time at the end of the 18th century by Borelle in Manchester and Papillon in Glasgow and that the latter's process proved to be the best. As the French method of dyeing Turkey Red had already been given to the world in a French government publication of 1765, it seems most likely that what those two Frenchmen brought to Britain was not the method itself but the "know-how" necessary for its successful commercial application.

A little information about Wilson is given on pp. 27 and 28 of *A Contribution to the History of the Township of Ainsworth* by Robert Muschamp [Bury ca. 1930], a copy of which was given recently to the Society's Committee for the Preservation of Historical Records by Mr. Abraham Lomas of Ainsworth House, Breightmet, Bolton. Wilson gave two lectures on dyeing to the Manchester Literary and Philosophical Society, his book being based on them, and he was presumably the John Wilson whose name appears among the list of members in Volume I of that Society's Memoirs published in 1785, in which case he was one of the earliest if not a founder member of that Society, to whose work at that and subsequent times the dyeing and finishing industries owe so much.

<div align="right">Yours truly
C. O. CLARK</div>

THE PRIORY
    BOLTON
      BRADFORD
        YORKS.

29th September 1950

ERRATUM

Open-width Dyeing Machine. J. Dungler. (J.S.D.C., **66**, 444 (Aug. 1950))—The number of the patent should be *B.P.* **636,554**, not "636,544".

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 12th July 1950, the proceedings included the following items of interest—

FESTIVAL OF BRITAIN— Dr. H. W. Ellis was authorised to give, on behalf of the Society, technical advice and assistance to the Council of Industrial Design in the staging of exhibits concerned with dyes and dyeing.

HISTORICAL RECORDS COMMITTEE — It was reported that Mr. K. G. Ponting had accepted Council's invitation to serve on this Committee.

SCHWEIZERISCHER VEREIN DER CHEMIKER-COLORISTEN— A letter was read from Dr. G. H. Lister conveying the cordial greetings and best

wishes of the Swiss society from their President, Dr. H. Ris, and the assurance that members of the Society of Dyers and Colourists in Switzerland would be heartily welcomed at meetings of the Swiss society. It was resolved that a suitable reply should be sent.

MEMBERSHIP— Six applications for ordinary membership were approved.

Deaths of Mr. E. B. Adams, Mr. H. Mennell, and Mr. C. Sandiford

We regret to report the loss by death of Mr. E. B. Adams, Mr. H. Mennell, and Mr. C. Sandiford, the first-named a member of the Committee on the Dyeing Properties of Vat Dyes.

Meetings of Council and Committees
September

Council— 20th
Publications— 19th
Dyers' Company's Medal— 20th

Conference at Harrogate
19th-22nd September 1951

The Society is planning to hold a conference at Harrogate on Wednesday–Saturday, 19th–22nd September 1951. It will be run on the lines of the Symposium on Photochemistry in relation to Textiles held in September 1949, but there will be no duplicate sessions. There will probably be seven sessions, on the Wednesday, Thursday, and Friday morning and afternoon, and on the Saturday morning, each devoted to a survey of the evolution of the manufacture and application of one of the main classes of dyes. It is hoped that preprints of papers will be available before the date of the meeting; thus, lecturers will need to give only brief accounts of the salient features of their papers, so that most of the time will be available for discussion.

Annual Meeting of Swedish Dyers

The Annual Meeting of Svenska Färgeritekniska Riksförbundet (the National Association of Swedish Dyers and Colourists) was held in Stockholm on 26th and 27th August 1950. Papers were read by Mr. G. S. J. White, a member of Council, on Nylon Dyeing, and by Dr. R. Christ on Continuous Dyeing. The Association extended its hospitality to Mr. F. Scholefield, our President, who conveyed the Society's greetings and expressed the hope that members of the Swedish Association would take an increasing interest in the activities of our own Society. The Chairman, Mr. Agaton Mars of Borås, expressed his pleasure at the presence of Mr. White, Dr. Christ, and Mr. Scholefield, and presented them with the Association's badge.

New Books and Publications

The Examination of Damage in Wool

Parts I and II by A. D. J. Meeuse, H. A. J. Hietink, and C. J. Gorter. Pp. 18 + 7 tables + a list of 292 references. Part III by A. D. J. Meeuse. Pp. 27. Supplement, 43 figures + 4 diagrams + 8 tables. Publication No. 97 of the Vezelinstituut T.N.O. Delft. 1950. Price, 18 Dutch florins.

The problem of detecting and estimating damage in wool materials has attracted the attention of many investigators, largely on account of its industrial importance, but in spite of the great deal of work which has been done there is still no completely satisfactory method. The literature on the subject is scattered about in many journals, some of which are difficult to obtain, and there was need for a comprehensive summary of the position at the present time. This has been provided by Parts I and II of the book under review, which is a contribution from the Vezelinstituut of Delft. The various methods are grouped together in tables under the following headings— examination of changes in morphological characteristics of fibres, histochemical examination, swelling phenomena, chemical analysis including dyeing tests, physicochemical tests, and physical properties. Each table is accompanied by a critical commentary, in which are summarised the published observations on each of the tests mentioned and also previously unpublished comments by workers at the Vezelinstituut. The tables are preceded by a discussion of the various aspects of the problem, and useful information is given on cumulative damage and on the causes of damage. Much of the difficulty in assessing the significance of the various publications arises from the different meanings attributed to the word "damage". In the present volume the following definition is adopted—

"Wool is damaged if the amount of damage is so much higher than the usual percentage for that particular type of wool that the serviceability is impaired or undesired effects are encountered either during later stages of the manufacturing process or during the actual use of the finished goods."

In Part III a description is given of a qualitative method developed at the Vezelinstituut for estimating damage in wool, involving microscopic examination of the fibres in water, in solutions of methylene blue and of methyl orange, and after treatment with a solution of caustic potash in ammonia (Krais–Markert–Viertel test) or with saturated bromine water (modified Allwörden test). The method has been used successfully in routine work, and twelve examples of its application are given. The text is illustrated by photomicrographs collected together in the supplement. Sufficient experimental details are supplied to enable other workers to apply the tests, and it would be interesting if their findings could be reported in the near future. The whole work constitutes a valuable contribution to a very complex problem.

C. S. WHEWELL

Technique of Organic Chemistry
Volume III

Edited by A. Weissberger. Pp. ix + 661. London and New York: Interscience Publishers. 1950. Price, 80s. 0d. or $10.00.

This volume continues a series of texts intended to contribute to the better understanding and more rational application of various techniques available for use in the investigation of organic compounds. The subjects discussed are— (i) Heating and Cooling, (ii) Mixing, (iii) Centrifuging, (iv) Extraction and Distribution, (v) Dialysis and Electrodialysis, (vi) Crystallisation and Recrystallisation, (vii) Filtration, and (viii) Solvent Removal, Evaporation, and Drying.

Though a member of a lengthy series, this volume is worth consideration on its own merits.

So far as can be judged from the publisher's announcements for future volumes, the present text covers the majority of the "separation techniques" other than distillation and adsorption. Together with the volumes on these subjects, it will probably prove the most valuable part of the series for the reader of wide interests. The remaining volumes appear to be far more restricted in scope, and presumably considerably more detailed in presentation. The authors of the respective chapters in the present book have valuable information and comment to offer on each subject, and it may be remarked that there is no reason why their readers should be limited to workers in organic chemical laboratories. The subjects and their treatment are common to most laboratories interested in separation processes or other unit operations.

A comparison of the detail and selection shown in each section of the text indicates the difficulty inherent in such compilations in fixing the presumed ability and knowledge of the reader. It is perhaps wise to consider such books merely as sources of methods which present sufficient evidence on each to encourage, or discourage, the reader in attempting their use. While any laboratory worker should be able to comprehend, and use, the simplicities of heat transmission, for example, there are techniques which must be carried out at research level to be of any value. The operator would then depend for his information on a detailed study of the particular field, and for his purpose the present type of compilation might serve only as an introduction. Depending on its limitation in the choice of subjects, the technique text is thus liable to be judged by two standards— how far it assists the operator on methods which are of general use for short-term application, and how far it aids a reader in assessing the use and limitations of specialised techniques which involve the laboratory organisation in the provision of specialised labour and semi-permanent installations of apparatus. It is perhaps to the credit of the editor and authors that the present text includes instances from both classes so skilfully incorporated that the reader is deluded into considering all techniques as being equally simple. The chapter on each subject is liberally supplied with references,

essential in such a compendium, and from these the operator will ultimately detect difficulties in those methods which require extensive reading prior to attempting the practice.

The major criticism against this text arises from the scope attempted. It is likely that this has been extended unreasonably when the same book discusses the theoretical relationships expressing the movement of material through a semi-permeable membrane and also describes in detail, with illustration, the Bunsen burner. The presumed scientific status of the reader is by no means clear, and the book gives the impression that it is intended as a reference for the whole laboratory organisation, from the Research Director down to the recently recruited Laboratory Assistant. This apparent width of purpose is a weakness, though it is only fair to add that each member of the organisation may well value this book, so long as each does not hope for identical assistance from it: If this occasionally ill-judged allocation of space and endeavour is overlooked, the book can be considered a valuable addition to any laboratory bookshelf. That is its place: as a source-book for encouraging the consideration of valuable techniques which repay periodic assessment in terms of present problems. The reader of more general interest would probably have welcomed further critical comment on the methods; for instance, the variations on a technique, or adaptations of equipment, should have been reviewed collectively, so that their relative scope and usefulness become more evident.

As the editor comments, "the field is broad and difficult to survey", and it is thus commendable that in a text giving admirable descriptions of apparatus space has been retained for the theoretical considerations underlying each technique. The necessarily limited presentation of these theories is unsatisfactory in some cases, but the text will serve its purpose in guiding the reader and suggesting the limits of further study required in any particular application, While explaining the theoretical background sufficiently to give confidence in attempting, or extending, the practice to new problems, the development and details of apparatus are discussed adequately to serve as a valuable constructional guide. J. A. STORROW

Reports on German Industry

I.G. Farbenindustrie A.-G.
Research Reports on Intermediates 1939
FD 2731/49* (PB 14,999).

Microfilms of papers written in German in 1939—

WOLFEN

(1) *Separation of Furfuraldehyde from Sulphite Waste Liquor*
(2) *Experiences with Raney Catalysts in Hydrogenation*
(3) *5' - Aminonaphthyl - 5 - hydroxynaphthiminazole - 7 - sulphonic Acid and its Derivatives*
(4) *N-Aryl-3-hydroxypyrrolidine*

(5) *Menaphthyl-S Acid (1-Methyl-4-amino-5-hydroxy-naphthalene-1'-sulphonic Acid), and iso-S acid (1 - Methyl - 4 - hydroxy - 5 - aminonaphthalene -1'- sulphonic Acid).*

WOLFEN

FD 2732/49* (PB 14,999).
(1) *3:4:5:6-Tetrachloro-2-aminophenol*
(2) *N-Butylhydroxyquinolone*
(3) *Diphenylamine Derivatives*
(4) *9:10-Dihydroacridines*
(5) *p-Dichlorobenzene*
(6) *Chlorination of isoButylene*
(7) *Cation-exchange Resins from Ligninsulphonic Acid.*

MERSEBURG, UERDINGEN, AND WOLFEN

FD 2733/49* (PB 14,999).

(1) *Production of Mesitol (1:3:5-Trimethylphenol) by Alkaline Oxidation of the Alcohol Fraction 200–250°c. of isoButyl Oil*

(2) *Dye Intermediates from Allylphenols*

(3) *High-pressure Tube Processes.*

LUDWIGSHAFEN
4:4′-DICHLOROBENZOPHENONE—
2-AMINO-5-CHLOROBENZOIC ACID

FD 2735/49* (PB 14,999).

(1) *Separation of 4:4′-Dichlorobenzophenone from Crude Dichlorobenzophenone by Partial Sulphonation—Determination of the 4:4′-isomers in technical products*

(2) *4:4′-Dichlorobenzophenone Chloride*

(3) *Large-scale Production of 2-Amino-5-chlorobenzoic Acid*

LUDWIGSHAFEN

FD 2737/49* (PB 14,999).

(1) *cycloHexanone from Phenol and its Oxidation to Adipic Acid*

(2) *Enolisation of Crotonaldehyde*

(3) *Butanepolycarboxylic Acids*

(4) *Derivatives of 2-Butene-1:4-diol.*   C. O. C.

I.G. Farbenindustrie A.-G.
15th AKo (Azo Commission) Meeting
Frankfurt a. M., 20th April 1940

Microfilms of reports, written in German, submitted by the various works on their activities in the azo field during the previous year—

LUDWIGSHAFEN

FD 310/50*.

Many chrome dyes from 2-naphthylamine-3-carboxylic acid and its sulpho derivatives are sensitive to the method of afterchroming, but 4-chloro-5-nitroaminophenol-azo-2-naphthylamine-6-sulpho-3-carboxylic acid and 4-sulpho-5-nitroaminophenol-azo-2-naphthylamine-3-carboxylic acid are both vivid greens of good fastness properties and suitable for commercial use. The chrome complex of 4-sulpho-6-nitroaminophenol-azo-2-naphthylamine-3-carboxylic acid was proposed as a vivid green addition to the Palatine Fast range. The results of numerous trials on the dyeing of nylon and Perluran fibres are given. A range of water-soluble acetate rayon dyes including Celliton Fast Blue FW is described.

LEVERKUSEN

FD 311/50*.

The topics dealt with include—

(1) Diaminopyrazoles from substantive hydrazines—Supranol yellow dye

(2) Benzo Fast Copper Blues

(3) A dark blue and a greenish-yellow acetate rayon dye

(4) Dye for mixed fibres

(5) Benzo Fast Chrome Orange

(6) Aminonaphthols treated with aromatic di*iso*cyanates as intermediates for azo dyes

(7) 6-Sulpho-1:8-aminonaphthol-azo-*m*-phenylene-diamine

(8) Work on improving para, Benzoform, and acid dyes.

MAINKUR

FD 312/50*.

A 13-pp. report dealing with acid, chrome, and direct dyes. The manufacture of various dyes of the Supramine and Supranol classes is described, as well as work on improving the fastness to steaming and light of Sulphon-cyanine Blacks and Nerol Blacks. The constitution of various chrome olives is given, one of which was to be sold as Diamond Olive GL, as well as of a number of brown, grey, or khaki afterchrome dyes. The dye—

3-Amino-4-hydroxydiphenyl sulphone→
      1-*o*-Sulphophenyl-3-phenyl-5-pyrazolone

is extremely fast to light. Many new intermediates for direct dyes, particularly aryl derivatives of M acid, had been investigated and patents claimed for them. Direct dyes prepared from acylated benzidinemonosulphonic acid

showed promise, and much work had been done on direct dyes of good fastness to light. Several dyes had been prepared to compete with Chlorantine Fast Yellows, but all proved to be unsatisfactory.

LEVERKUSEN

FD 313/50*.

An 18-pp. report. In the acid group dyes from chlorinated aminophenyl benzyl ethers and dichlorobenzoyl-K acids were compared with the corresponding dyes from chlorinated aminodiphenyl ethers and with Carbolan Crimson BS. Those from the phenyl benzyl ethers were slightly less fast to light than those from the diphenyl ethers. In the range—

Chlorotoluidinesulphonic acid→Acetyl-I acid

dyes with the Cl *ortho* to the azo group were completely destroyed after 14 days' exposure to sunlight, the others being unchanged. 4-Phenyl-1-naphthol-3-carboxylic acid proved of little use as a coupling component for dyes to stand afterchroming. An account is given of investigations into the 1-phenyl-1-pyrazolone(5)-4-sulphonic acids and their derivatives. In the direct field special study had been made on the effect of definite variations in constitution and dyeing behaviour. In the Congo Red and Benzo Fast Scarlet range it was concluded that the position of the methyl group has a big effect on both substantivity and aggregation in the dyebath, increased fastness and best colour value being obtained by dyeing at high temperatures. Considerable work had been done on stilbene and azoic dyes and pigments. A scarlet of good light fastness and other properties was obtained by phosgenation of 1:8-nitroaminonaphthalene-3:6-disulphonic acid→2:5-dimethoxyaniline.

HOECHST

FD 314/50*.

PIGMENTS— Because of its purity, extreme fastness to light, and insolubility in solvents—

3:3′-Bistrifluoromethylbenzidine⇄Acetoaceto-*m*-xylidide

is very useful in printing inks and for colouring rubber and synthetic resins. Combinations of naphthol with 5-nitro-2-anisidine, 4-nitro-2-chloroaniline, and similar compounds yield oranges and yellows of better light fastness than the corresponding Hansa pigments. Pigments based on Fast Scarlet VD base showed no advantage over existing commercial products. Pigments made with 3-halogeno-1-aminoanthraquinones as the base had surprising clarity and excellent fastness to light. Good results in yarn dyeing had been achieved by coupling Naphtol AS brands with 3-bromo-1-aminoanthraquinone instead of the usual 1-aminoanthraquinone.

DIKETEN DYES— Much work in this field is described dealing with direct and chrome dyes and pigments. A greenish-yellow dye—

Dehydrothiotoluidine-3′-sulphonic acid→
   1-Acetoacetamido-2-methoxybenzene-5-carboxylic acid

was proposed to supplement Sirius Yellow G. A suggested Dianil Yellow brand was dehydrothiotoluidine-7-sulphonic acid coupled with its acetoacetyl derivative or with 4-acetoacetylaminoazobenzene-1′-sulphonic acid. Work had also been done on greens from similar intermediates.

WOOL DYES— Several dyes of the Carbolan, Palatine Fast, and chrome types were prepared, but none equalled existing commercial products. Use of *o*-aminomandelic acid as an intermediate for azo dyes showed that the mandelic acid group as such does not enable formation of a chromium complex, nor is the carboxyl group of the mandelic acid necessary for the chromability of the dye.

COTTON DYES— The urea from—

4-ω-Sulphopropionylamino-1-aminobenzene→
         m-Aminoacetanilide

has better dischargeability and light fastness than Diphenyl Fast Yellow GL. Of new Benzo Fast Copper dyes—

Salicylic acid←Benzidine→Resorcinol←*o*-Amino-
                sulphosalicylic acid

a red–brown, was proposed to be added to the commercial range.

DYES FOR WOOL–VISCOSE RAYON MIXTURES— Much work had been done in this field and the constitutions of the following are given—

Autazol Chrome Navy Blue BRA
Autazol Chrome Salt R
Nitrazol Black 81967 for Wollstra
Wollstra Blue Black 76556
Wollstra Chrome Blacks 79613/41 and 79609/42
Wollstra Dark Brown 76557.

ACETATE RAYON DYES— The following self-couplers were prepared—

(1) 1 - *m* - Aminophenyl - 3 - methyl - 5 - pyrazolone, for yellow (Patent Application I.60,551)
(2) Naphtol AS–BS, reduced with Na₂S, for red (Pat. Appl. I.60,800)
(3) *m* - Aminophenol → 1 - *m* - Aminophenol - 3 -methyl-5-pyrazolone, for orange (Pat. Appl. I 63,047)
(4) *p* - Aminoacetanilide $\xrightarrow{\text{Acid}}$ 1 - Amino- 7 - naphthol, saponified, for brown (Pat. Appl. I 63,047).

2-Aminothiazole, compared with 6-methoxy-2-amino-benzothiazole as an intermediate, gives products which yield much clearer and yellower dyeings, and which are slightly less fast to wet processing and much inferior in fastness to light.

WOLFEN

FD 315/50*.

LEATHER DYES— The ditaurines of aromatic amine bases combined with halogenonitroanilinesulphonic acids yield yellow–browns of good general and excellent wet fastness.

2-Chloro-6-nitroaniline-4-sulphonic acid→
Diethyl-*m*-toluidine

(for which Pat. Appl. I 64,529 had been lodged) is a red of excellent penetrating and good fastness properties.

DIRECT DYES— Diazo Fast Green GFL had been found to be particularly suitable for *para* development, and a range of black dyes had been prepared surpassing the existing ones in fastness to light and washing and in dischargeability.

BENZO FAST COPPER DYES— Work is described on yellows, oranges, and reds.

ACETATE RAYON DYES—
2:6-Dichloro-1-amino-4-nitrobenzene→
3-*N*-Methyl(or ethyl)phenylamino-1-butanol

was suggested as a faster-to-light replacement for Celliton Fast Brown 3R. Celliton Fast Red GG had been replaced by—

p-Nitroaniline→3-*N*-Ethylphenylamino-1-butanol

as the latter is faster to light. Work is also described on black and brown Cellitazols.

SUDAN DYES— Much work had been done on the influence of various components on light fastness and solubility.

OFFENBACH

FD 510/50*.

Aminobenzenesulphonamides used as components for solvent-soluble dyes resulted in products of poor fastness to light. Coupled with 2:3-hydroxynaphthoic arylides, aminobenzenesulphonamides yield vivid orange and red dyes of good light-fastness but low tinctorial power, although their use was proposed for viscose rayon. Replacement of the sulphonamides by the corresponding carboxyamides resulted in better tinctorial power but lower fastness to light. Work had been done on the addition to the Vulcan range of an ultramarine and of a red similar to Vulcan Fast Red BF but resistant to alkali. Efforts had been made to increase the wet-fastness of existing acetate rayon dyes.

OFFENBACH— NAPHTOLS

FD 511/50*.

The composition is given of the following new or improved products placed on the market in 1939 and early 1940—

Non-dusting types of Fast Scarlet Salt VD and Variamine Blue Salt B, BA, FG, RT, and RTA
Fast Salts— Bordeaux 46061, Brown V, and Red SW
Naphtol AS–SK, 30726, and 31855
Naphtol AS, BO, BS, ITR, OL, and SW as "fine" brands which were readily soluble and resistant to hard water

Rapidogen Bordeaux RN, Brown IRRN, and Developer NF, NK, and NN.

The composition of the following competitive products is given—

Aizen Fast Violet Salt RH (Hodogaya)
Base du Rubis solide NS (Kuhlmann)
Orange Base Ciba V
Orange Salt Ciba V
Pharmasol Blue GNXX, Bordeaux BN, Brown GN, Red RN.

Work is described on various bases and Naphtols, and a list of I.G. German patent applications in this field is given. Work had also been done on Naphtols for dyeing wool–viscose rayon mixtures and as self-couplers for acetate rayon. A patent application is given for a method of rendering water-soluble dyes insoluble after application to the fibre; it had not been successful with Naphtols, but had been found of use for printing with phthalocyanines.

C. O. C.

I.G. Farbenindustrie A.-G.
16th AKo (Azo Commission) Meeting
Hoechst, 12th December 1941

Microfilms of reports, written in German, submitted by the various works dealing with work done in the azo field during the previous 18 months—

LUDWIGSHAFEN
CHROME DYES FROM *O*-CHLOROAZO DYES AND 8-AMINOQUINOLINE

FD 512/50*.

A 6-pp. paper by Pfitzner describing work which led to the filing of *G.P.* Appl. I 65,231 for *o*-quinolylamineazo dyes. 2-Chloroaniline-5-sulphonic acid→*p*-Cresol reacts with 8-aminoquinoline to yield a dye which is superior to Metachrome Olive Brown G, especially as regards light fastness.

LUDWIGSHAFEN
NEUTRAL-DYEING METALLIFEROUS DYES

FD 513/50*.

A paper of 11 pp. by Pfitzner. Dyes containing sulpho groups can be metallised in acid amides or in ammonium salts of carboxylic acids, the products being purer than those obtained by the customary method in aqueous medium. A *G.P.* application (J 70,529) had been based on this discovery. The chrome complexes of the following dyes had been prepared in this manner— Zapon Fast Black Pf 170b, Orange RE, Red BE and GE, and Yellow R, the constitution being given in each case. In the Cr, Co, and Fe complexes one metal atom links two dye molecules. Dyes of this type free from sulpho groups readily dye nylon from aqueous dispersion to give dyeings of good wet fastness and of light fastness equal to that of Palatine Fast dyes. They are applied from a neutral bath and do not change in hue on washing; they are also completely independent of the acid-binding capacity of the nylon. Their use was claimed in *G.P.* Appl. J 67,012. Introduction of sulphonamide groups improves their water-solubility (*G.P.* Appl. J 67,824).

Azo and azomethine dyes metallised in this manner and free from sulpho groups dye wool from a neutral bath to yield level dyeings of good fastness to rubbing and satisfactory fastness to light and wet processing. The results of tests made on 18 such dyes (the constitutions of which are given) are described. Their manufacture and application were claimed in *G.P.* Appl. J 70,346. Their levelling properties were much enhanced by use of Palatine Fast Salt O, and many of them give satisfactory exhaustion at 80°c.

LUDWIGSHAFEN
COTTON DYES CAPABLE OF BEING METALLISED

FD 514/50*.

A 15-pp. paper by Diebold describing dyes containing the *o*-hydroxycarboxy and other groups capable of forming metal complexes. The mechanism of this action is explained, and a method described of treating the dyes in substance or on the fibre in a single bath containing both copper and chrome. This treatment considerably increases fastness to washing and to light. *G.P.* Appl. J 69,797 and J 70,853 covered its use.

LUDWIGSHAFEN
ERGANIL AND BENZO FAST CHROME DYES

FD 515/50*.

ERGANIL DYES by Neumann (3 pp.) — Work is described on the production of some grey dyes of the Erganil series, which though cheap to make and fast to mineral acids had been rejected by the sales staff as having insufficient penetrating power.

BENZO FAST CHROME DYES by Neumann (9 pp.) — Special study had been made of the use of carboxydinitrostilbene derivatives as intermediates. As a result Benzo Fast Chrome Orange R had been produced. Half-wool Metachrome Orange R was a mixture of the former with Metachrome Orange R. A bordeaux superior in fastness to light and wet processing to those already available had also been prepared. Benzo Fast Chrome Rubine 26,385—

p'-Aminobenzoyl-p-aminosalicylic acid→

m-Toluidine→Acetparamine-J acid urea

was used as the direct component of Half-wool Metachrome Rubine 3BW.

Dyes from amines containing the grouping –R·NH·CO·R– prepared by coupling aminobenzoylated amines or diamines with derivatives of salicylic acid, while otherwise good, lacked fastness to light. The dye—

Parazole-GP base→Salicylicsulphonylmethyl-J acid

was the first homogeneous half-wool metachrome dye that had been produced.

BENZO FAST CHROME BLUES by Diebold (15 pp.) — Work which led to G.P. Appl. J 62,031 and J 69,516 is described. Benzo Fast Chrome Blue FG—

p-Amino-o-sulphosalicylic acid→1:7-Cleve
acid→1:6-Cleve acid→Phenyl-J acid

mixed with Alizarin Chrome Blue FFR yielded Half-wool Metachrome Blue GW.

LUDWIGSHAFEN
ZAPON FAST DYES

FD 517/50*.

ESTER-SOLUBLE ZAPON FAST DYES by Krzikalla (5 pp.) — Work is described which led to the filing of G.P. Appl. J 67,354 covering the imparting of increased solubility in esters by introducing aliphatic side-chains into metalliferous azo dyes.

COBALT-COMPLEX AZO DYES CONTAINING SULPHO GROUPS by Pfitzner— The dimethyl palm kernel fatty amine salt of the complex cobalt compound of—

4-Nitro-2-aminophenol-6-sulphonic acid→
1-Phenyl-3-methyl-5-pyrazolone

had been proposed as an orange for the Zapon Fast range. The 1 : 1 (Co : dye) complexes are also purer in hue and faster to light than the 1 : 2 complexes. The 1 : 1 complexes dye wool but their levelling power is very poor, so that they cannot compete with Palatine Fast dyes.

LUDWIGSHAFEN
WATER-SOLUBLE ACETATE RAYON DYES

FD 518/50*.

A paper by Neumann (8 pp.). Dyes containing carboxyl groups depend for their dyeing power on the addition of salts. Dyes containing esterified carboxyl groups are independent of addition of salts but lack solubility. By using mixed couplings it was found possible to combine the advantages of both types without their drawbacks becoming noticeable. The following five dyes of this type were being put into production—

Acetate Rayon Scarlet 3892

4-Nitroaniline→0·7 mol. Methylanilinepropionic acid
+ 0·4 mol. Hydroxyethyl methylanilinepropionate

Acetate Rayon Red 4139

4-Nitroaniline→0·7 mol. Ethyl-m-toluidinepropionic acid
+ 0·3 mol. Hydroxyethyl ester

Acetate Rayon Rubine 17440

2-Chloro-4-nitroaniline→0·7 mol. Ethyl-m-toluidine-propionic acid + 0·3 mol. Hydroxyethyl ester

Acetate Rayon Red Violet 5739

2:4-Dinitroaniline→0·7 mol. Methyl-m-toluidinepropionic acid + 0·3 mol. Hydroxyethyl ester

Acetate Rayon Brown 25139

2:5-Dichloro-4-nitroaniline→0·7 mol. Methyl-m-toluidinepropionic acid + 0·3 mol. Hydroxyethyl ester.

Examination of some Swiss and British patents is described; the work done on one of the British patents led to the preparation of the first known direct-dyeing water-soluble acetate rayon black.

LUDWIGSHAFEN
LUMOGEN FLUORESCENT DYES

FD 519/50*.

β-Naphtholaldehyde by the Gattermann Synthesis by Mühlbauer (6 pp.). — Two processes for the preparation of this intermediate are given.

Lumogen L Bright Yellow (2:2'-Dihydroxynaphthaldazine) by Mühlbauer (11 pp.).

Lumogen L Yellow Orange (2:2'-Dihydroxybenzaldazine) by Mühlbauer (8 pp.).

Aldazines of Aromatic Hydroxyaldehydes and their Fluorescent Properties by Mühlbauer (56 pp.). — The primary object of the work described was to find substances having great luminosity, good fastness to light, and white fluorescence. Compounds having the first two properties were found, but none with the third; however, combinations of luminous substances could be made to give white fluorescence. It was found that simple aldehydes formed aldazines when treated with hydrazine, though these had no fluorescence, but that substituted aldehydes, especially the hydroxyaldehydes and particularly the o-hydroxyaldehydes, yielded aldazines of satisfactory fluorescence. The free hydrogen of the hydroxyaldazine is essential for fluorescence. When it is substituted then fluorescence disappears. Presence of an unbroken chain of conjugated double bonds is an indication but not a cause of fluorescence. The mechanism of fluorescence is fully explained. The preparation and properties of a large number of hydroxyaldazines are described.

LUDWIGSHAFEN
ANALYSIS OF COMPETITORS' DYES

FD 520/50*.

Constitution of New-type Zapon Fast Dyes of Competitors by Kirsch (12 pp.) — Analysis of Scarlet BB for Nitrolacquer (Ciba) (Swiss P. 186,548, 188,525–7; and B.P. 460,725 (J.S.D.C., 53, 256 (1937)).

Chromiferous Dyes of Acna (Stenamina Dyes) and the Italian Patent Position by Kirsch and Werniger— Analyses are given of Stenamina Blue 2G, Bordeaux R, Green S, Red BR and R, Violet B, and Yellow B and R. The green was covered by Ciba's Italian P. 246,153, while the others were either covered by Italian Patents of the I.G. or were not protected. A copy of the agreement made between I.G. and Acna regarding the Stenamina dyes is given.

OFFENBACH

FD 521/50*.

A 10-pp. report. Presence in monoazo dyes of sulphonamide and carboxyamide groups, both the amide hydrogen atoms of which are substituted, increases solubility in organic solvents. Alcohol-soluble dyes for rubber printing can be prepared from bases containing a carboxydibutylamide radical. Bases containing sulphonamide or carboxyamide groups yield vivid dyes when coupled with naphthols. The kind of substituent in the amide radical is important, the most useful being dipropyl, butyl, and "cycloxyl". Dyes which do not bleed in white rubber include those in which m-aminobenzamides substituted by CH₃, alkoxy, or halogen in the 2:5-position to the amino group are used as diazo components. The resulting shift to blue can be reversed by substituting hexahydrophenyl for phenyl in the carboxyamide group. Formulæ for several such dyes are given. Various combinations were tried as dyes for Igelit, but only a brown had been found to be of any use. Constitutions and properties of a number of pigments for use on rayon are given, as well as of several imparting lustre to acetate rayon and for pigment printing.

HOECHST

FD 522/50*.

PIGMENTS— Work is described on yellows suitable for yarn dyeing and on new Hansa Yellows. A series of pastes

for use with a new binder for aqueous pigment printing had been developed.

ACETATE RAYON DYES— ω-Phenylaminoacetanilide and ω-phenylaminoacetophenone and their derivatives had been tested as coupling components for Celliton dyes. The constitution of a dye redder in hue than Celliton Orange GR, but having the same water, wash, and acid fastness, is given.

WOOL DYES — 3-Chloro-2-aminotoluene and 3:5-dichloro-2-aminotoluene coupled with pyrazolonesulphonic acids yield clear yellow dyes of excellent light fastness. Supranol Yellow 4G was to be replaced by—

o-Aminophenyl 4-hexyl ether→5-Chloropyrazole acid.

Dyes with pyrazolones from 1-amino-3- or -4-ω-sulphoacetylaminobenzene were of no importance. A chrome yellow with 1-amino-3-ω-salicylsulphonacetylaminobenzene as initial component had good fastness to light and to wet processing.

COTTON DYES— The following had been put on the market—

Dianil Yellow 3GW

Dehydrothiotoluidine-7-sulphonic acid→Acetoacetyl-dehydrothiotoluidine-7-sulphonic acid

Dianil Yellow GW

4:4'-Diaminodiphenylurea-3:3'-disulphonic acid$\rightarrow$̰
4-Acetoacetylamino-1:1'-azobenzene-4'-sulphonic acid

Benzo Fast Copper Brown BRL

Salicylic acid←Benzidine→Resorcinol←3-Amino-2-hydroxy-5-sulphobenzoic acid

The formula of a new Dianil Orange is given.

DYES FOR WOOL–VISCOSE RAYON MIXTURES— Much work in this field, particularly in the Autazol Chrome range, is described together with relevant patent applications.

WOLFEN
FD 523/50*.

WOOL DYES— Work on dyes leaving cotton and rayon a pure white is described. Other work led to the production of—

4-Aminodiphenyl-4'-sulphanilide→1-(2'-Chloro-5'-sulphophenyl)-3-methyl-5-pyrazolone

a neutral-dyeing yellow for wool said to be superior to any British or Swiss product.

LEATHER DYES— Yellow–browns of good fastness are described.

DIRECT DYES— Work on blacks is described and tabulated.

ACETATE RAYON DYES— Blue dyes superior tinctorially to Celliton Discharge Blue 2RF had been produced, and a new series of aromatic bases which on coupling yield products of excellent clarity and fastness to light.

SUDAN DYES— A new series of reddish browns of excellent light fastness, solubility in hydrocarbons, and resistance to sublimation is described.

TRIAZOLE BASES— Methods of preparation are briefly indicated, and a short account is given of how the mode of formation of the triazole may be used for determining how diazo compounds couple with m-aminophenol.

MAINKUR
FD 524/50*.

ACID DYES— Work in the Supranol range led to G.P. Appl. J 68,550. Other work was covered in G.P. Appl. J 70,493 and J 64,738.

CHROME DYES— Dyes prepared from 2-acetylamino-4-hydroxythiazole were all unsatisfactory, as were many prepared from glyoxal and dihydroxynaphthalenes. Introducing the benzyl or o-chlorobenzyl radical instead of phenyl into Diamond Olive GL—

4-Nitro-2-aminophenol→Phenyl-1:7:3 acid

increased the vividness and gave good hues in artificial light but slightly lowered the fastness to light.

ACETATE RAYON DYES— G.P. Appl. J 63,645 and J 64,417 covered new yellows, oranges, and reds, one of them—

Bishydroxyethyl 1-amino-4-isophthalate→Dimethylaniline

was a fast-to-light orange giving better penetration than Celliton Orange GR. G.P. Appl. J 70,233 and J 70,398 covered dyes using ω-hydroxybutylanilines as components;

they are faster to light and wet processing than those derived from hydroxyethylated bases.

DIRECT DYES— Much work had been done on intermediates for Sirius dyes. G.P. J 67,053 and J 67,191 covered dyes from aryl-M acids, the greys of this series, which could be after-chromed or -coppered, being particularly valuable.

BENZO FAST COPPER DYES— The results of trying many new combinations are given. The only new product introduced was Benzo Fast Copper Grey BL—

γ acid←4-4'-Diaminodiphenyl-3:3'-dihydroxyacetic acid→Benzidyl-M acid

An account is given of attempts to produce a green for this range.

BENZO FAST-CHROME DYES— A great variety of compounds are described, the best being—

4-Aminosalicylic acid→δ-Cleve acid→Aminoquinol dimethyl ether→p-Anisyl-M acid

a strong neutral grey with a good hue in artificial light.

AFTERTREATMENT WITH COBALT SALTS— An almost full range of dyes for this aftertreatment had been produced; it is not suitable for all dyes, but good fastness is obtained with oo'-dihydroxy and o-hydroxy-o'-amino azo dyes.

OFFENBACH
NAPHTOL AS
FD 525/50*.

Work leading to the production of Rapidogen Navy Blue IB is described together with other work in the Naphtol field. As Fast Red Brown V base had given much difficulty in use, a more reliable method for the production of browns had been devised (G.P. Appl. J 67,434 and J 69,070–1). Swiss, French, and American patents in the azoic field are reviewed.

LEVERKUSEN
FD 526/50*.

Work on substantive dyes suitable for use with metachrome dyes was continued. New dyes of the Sirius Supra Red 5B type contain a salicylic acid group and are rendered more substantive by introduction of CO·NH groups; one of them was being used as the direct component of Half Wool Metachrome Red BW. 1-Aminocarbazole and its derivatives, coupled e.g. with resorcinol, yield metallisable dyes of inferior light fastness. Of the direct oranges having barbituric acid as the end component the following types are very fast to light—

C acid→m-Toluidine→m-Toluidine, amino-benzoylated→Barbituric acid

5-Sulpho-3-aminobenzoic acid→m-Toluidine→m-Toluidine, aminobenzoylated→Barbituric acid

and in fact surpass in fastness to light and in dischargeability the best products of the stilbene range. As a result of work on ureas from diaminostilbenedisulphonic acid, Blancophor R (1 mol. diaminostilbenedisulphonic acid treated with 2 mol. phenyl isocyanate) was being made. G.P. Appl. J 66,881 covered the manufacture of Supramine dyes having good wet fastness. A method of obtaining trichloroacrylyl chloride is given. This product was introduced into various azo dyes, giving them excellent fastness to washing on wool with slight loss in levelling power but little or no effect on light fastness. Efforts had been made to improve the wet fastness of Sirius Supra Yellow 5G by either enlarging the molecule or introducing a Cl atom into the coupling component occupying the meta position to the acetoacetamido radical. The constitutions of a new Benzoform Brown and Red are given.

LEVERKUSEN
AZO DYES— OXIDATION–REDUCTION POTENTIALS
FD 527/50*.

A 12-pp. report—

WOOL DYES— "Dimesylglycocoll" $(CH_3 \cdot SO_2)_2 N \cdot CH_2 \cdot COOH$ and its chloride were obtained by treating glycocoll with methanesulphonyl chloride. m- and p-Phenylenediaminesulphonic acids condensed with the chloride yielded diazo components which in turn yielded dyes superior in milling and perspiration fastness to the corresponding dyes from acetylphenylenediaminesulphonic acids, and of equal light fastness.

COTTON DYES— A new constitution for Curcumin S (Diamine Fast Yellow A) was proposed, and work on this constitution had led to the development of Diamine Orange GR (*G.P.* Appl. J 67,772). Methods of synthesising polyazo dyes free from auxochromes are described with the aid of structural formulæ. The polyazobenzenes are yellow to reddish-brown direct dyes of unusually strong resistance to oxidising agents. Arylhydrazine-β-sulphonic acids couple with diazo compounds in acid medium. The β-SO₄H group can be split off the products to yield free azophenylhydrazines, which can be condensed to pyrazolones. Dyes made from them are described. Hydroxyalkyl- and dihydroxypropyl-Cleve acid were tried instead of Cleve acid in making Pluto Black BB, but offered no advantage. Constitutions of a new Benzoform Blue and a Diazo Dark Blue are given.

LEATHER DYES— Dark blue to blue–black Erganil dyes, which in addition to leather-dyeing properties gave dyeings of good wet fastness on silk, are described. When filtering Direct Deep Black brands on a rotary filter the filter cloth often became clogged; this had been overcome by adding 0·1–0·5% gelatin (on weight of dry dye) to the liquor.

OXIDATION – REDUCTION POTENTIALS — A 36 - pp. theoretical discussion by Suckfüll. C. O. C.

I.G. Farbenindustrie A.-G., Wolfen

Microfilms of papers written in German in 1937—

METALLIFEROUS COTTON DYES

NAPHTOLS FOR WOOL–VISCOSE RAYON MIXTURES

FD 3177/48*.

(1) *Review of the Patents [granted (mainly to I.G. and Ciba) during 1912–37] in the Copper-complex Dye Field*

(2) *Attempts to render Chromiferous Dyes substantive to Cotton*

(3) *Substantive Azo Dyes from 3-Hydroxybenzidine*

(4) *Red Benzo Fast Copper Dyes from 4:4'-Diamino-3:3'-diphenoxyacetic Acid*

(5) *Cupriferous Sirius Dyes from the Pyrazolone of 2-Naphthylamine-5:7-disulphonic Acid*

(6) *Metalliferous Dyes from m-Amino-p-hydroxyphenyl Ethyl Sulphone*

(7) *Bispyrazolones as Coupling Components for Cotton Dyes*

(8) *Benzidine - oo' - bishydroxyacetic Acid → Phenyl - methylpyrazolone*

(9) *Cotton Dyes for Aftertreatment with Copper*

(10) *Grey Fast-to-light Cotton Dyes*

(11) *Benzo Fast Copper Dyes*

(12) *Dyes from Aminonaphthoic Acids*

(13) *Fast Dyeing with Chrome Dyes on Wool–Viscose Rayon Mixtures*

(14) *Fast Development Dyeings on Wool–Viscose Rayon Mixtures with Neutral Water-soluble Substantive Naphthols— II*

(15) *Naphtol AS Derivatives having Hydroxyalkyl Groups in the Arylide Radical.*

DEVELOPMENT DYES FOR COTTON

FD 3178/48*.

(1) *Dihydroresorcinol as a Developer for Diazotisable Direct Dyes*

(2) *Diazo Reds and Oranges*

(3) *[Improving Dischargeability in Direct Dyes by] Substituting Aminobenzoylated J Acids for Iminazole-J Acid*

(4) *N-Aminophenyl-J Acids, their Derivatives and Dyes*

(5) peri-*Diazo Dyes*

(6) *A Diazoindigo Blue corresponding to Diazamine Blue BR (S)*

(7) *Diazotisable Dyes giving Yellow on Development with β-Naphthol.*

LEATHER DYES

FD 3179/48*.

(1) *Leather Dyes having Aminobenzylsulphonic Acids as Components— II*

(2) *Igenal Brown IGG and PM*

(3) *A Black Leather Dye with Good Penetrating Properties*

(4) *Leather Dyes of Good Penetrating Properties*

(5) *Metalliferous Leather Dyes*

(6) *Acid Leather Dyes from Diphenylamine Derivatives*

(7) *Igenal Dyes*

(8) *Erganil Dyes*

(9) *A Dark Green of the Igenal C Series.*

ACETATE RAYON DYES

FD 3180/48*.

(1) *Acetate Rayon Dyes*

(2) *Water-soluble Acetate Rayon Dyes*

(3) *Water-soluble Yellow Dyes for Acetate Rayon*

(4) *Arylaminopropionic Acids as Coupling Components for Water-soluble Acetate Rayon Dyes*

(5) *Water-soluble Yellow Monoazo Acetate Rayon Dyes resistant to Mordants*

(6) *Water-soluble Acetate Rayon Dyes [having Diphenylaminecarboxylic Acid as a Component]*

(7) *Water-soluble Acetate Rayon Dyes— of the series— Nitroaminobenzenesulphonic acid→Unsulphonated basic benzenoid component*
Benzenoid nitroamino compound→Sulphonated basic benzenoid component

(8) *[Dyes to compete with British] Water-soluble Acetate Rayon Dyes (3 papers)*

(9) *Phenyl Aminobenzenesulphonates as Assistants in dyeing Cellulose Triacetate Rayon*

(10) *Azo Dyes for Acetate Rayon—* Translation of a Russian survey of British, German, and American patents and literature.

AZO LAKES

FD 3181/48*.

(1) *Sudan Dyes*

(2) *Double-tone Dyes for Printing Inks*

(3) *Fast Yellow Pigment for Cellulose Nitrate and Alkydal Lacquers to be applied by Spraying*

(4) *Azo Pigments from Acetylacetone and Benzoylacetone*

(5) *Two Pigments from 3-Amino-4-methoxy[phenyl] Trifluoromethyl Sulphone*

(6) *Relationship between Hue and Particle Size and Shape of the Dye 2:5-Dichloroaniline→Naphtol AS-G*

(7) *Hansa Yellow Pigments containing Carboxyl and Sulpho Groups*

(8) *Adsorption of Nitrogen on Dye Powders as an aid to determining their Fineness.* C. O. C.

Anorgana G.m.b.H., Glendorf/OBB.
Post Burgkirchen/Alz.
Dyes— Plastics

FDX 816* (PB 84,973; Microfilm C 5).

Microfilm copy, in German, of 19 reports on various plastics written in 1940–41 and 316 reports written in 1931–38 by I.G. chemists on dyes, mostly azo dyes, and covering their application to all types of substrates. In addition there are accounts of the investigation of competitors' dyes and patented processes. Information is given on the manufacture of the following I.G. dyes—

Acid Alizarin Bordeaux B, Red GL
Acid Anthracene Brown PG
Amido Black Green B
Artificial Silk Black G
Azol Printing Orange R
Celliton Fast Yellow 5E [? 5R]
Columbia Fast Black G
Cotonesol AB
Diazo Brilliant Blue BBLA, Orange 5G
Direct Fast Brown TWC
Ergan Indigo Blue R
Fast Lacquer Black NC
Metachrome Orange 4RL
Oxamine Black RN and RX
Palatine Fast Blue Black, Bordeaux BN, Orange RN, Red BEN
Peri Wool Blue B
Permanent Bordeaux F2R
Pyramine Orange 3G
Silk Fast Grey BB
Sirius Pink G
Trisulphon Brown B
Vulcan Fast Blue RF
as well as of many Rapidogens, Benzo Fast Copper, Ergansogas, Cellitazols, Cellitons, Supramines, Erganils, Igenals, Naphtols, etc. C. O. C.

Abstracts from British and Foreign Journals and Patents

(*The Titles of Patents are abridged and modified*)

I— PLANT; MACHINERY; BUILDINGS

Calculation of Steam Requirements in Winch Dyeing.
E. Wachendorff. *Melliand Textilber.*, 31, 430–431 (June 1950).

The methods whereby the steam consumption of winch machines may be calculated are given in detail. A comparison is made between the steam requirements of open and closed machines under a given set of conditions.
F. A.

Fire Danger with Fibre Dusts. W. H. Geck. *Melliand Textilber.*, 31, 332–334 (May 1950).

Factors influencing spontaneous ignition in atmospheres containing fibre dust are discussed.
F. A.

. PATENTS

Cold Lime–Soda Water Softening. J. F. Sebald and Worthington Pump & Machinery Corpn.
U.S.P. 2,502,349.

Densifying Carbon Black and other Finely Divided Flocculent Powders. R. W. Skoog, W. F. Seeger, and United Carbon Co. Inc.
U.S.P. 2,502,106.

Pelleting Carbon Black. L. J. Venuto and Columbian Carbon Co.
B.P. 640,661.
U.S.P. 2,500,968.

Pelleting Carbon Black. Columbian Carbon Co., W. B. Wiegand, and C. W. Sweitzer.
B.P. 640,565.

Pelleting Carbon Black. M. L. Studebaker and Phillips Petroleum Co.
U.S.P. 2,503,361.

Heating Continuously Running Tows or Wound Packages. C. de Brabander and American Viscose Corpn.
U.S.P. 2,502,129.

Warp Dyeing Beam. H. V. Lang.   *U.S.P.* 2,505,498.

A perforated cylinder is fitted over heads having flange portions as an integral part of them. These flanges project a substantial distance inwardly toward each other and have several bosses cast integral with the flanges and the head. The flanges are slotted longitudinally of the periphery of the head, so that not only is the perforated cylinder amply supported, but there will be free flow of the liquor through the flange and through the ends of the perforated cylinder.
C. O. C.

Machine for Laboratory Dyeings. Yorkshire Dyeware & Chemical Co. Ltd. and R. A. Carter. *B.P.* 640,557.

A machine which ensures that the fabric will be given as good or better agitation than that obtained by hand has a support for the fabric, the support being mounted for both axial displacement and rotation about its own axis and capable of being reciprocated as regards both axial displacement and rotation.
C. O. C.

Stopping the Travel of an Endless Length of Material.
G. J. Sinclair and United Piece Dye Works.
U.S.P. 2,504,882,
U.S.P. 2,504,883.

Device for stopping piece or warp dyeing, etc. machines so that a predetermined area of the warp or fabric may be inspected.
C. O. C.

Continuous Dyeing and Developing. B. V. Stec and Botany Worsted Mills Inc.   *U.S.P.* 2,501,480.

The fabric passes through primary and secondary dye-baths, passing through squeeze rollers between the two baths, and thence into a heated development chamber. In this chamber the fabric is led over the lowest of a series of separator rolls, and thence passes over one or more rolls carrying longitudinally extended slats. It is then led to the upper area of a chain-feed consisting of two or more spaced chains carrying between them spaced slats or bars which bear the fabric along. After leaving this feed, the fabric is carried downward and led over the second of the separator rolls, then up again to and over the chain-feed, and thence down to the third of the spacing rollers. The fabric moves in the same way to each of the separating rollers until the layers of fabric on the chain equal the number of spacing rollers used and the initial end of the fabric lies at the inside or lower face of the pile at the discharge end of the feed-chain. Here the fabric is led over a turning bar and out of the casing surrounding the chamber. This gives uniform dyeing and permits dye development to be adjusted as to time without altering the speed of the machine, by simply changing the number of separator rollers and hence the number of laps built up upon the feed-chains before the turning and discharge movement of the fabric from the machine.
C. O. C.

Continuous Processing Machine for Cloth. W. M. Wentz and Du Pont.   *U.S.P.* 2,505,657.

The material to be dyed, etc. is fed continuously around slatted reels or drums in a number of laps, so that it may be treated for a long time in an apparatus taking up little space, with a very short liquor, and passed as many times through the liquor as desired. The laps are carried on a continuous conveyor having transverse raised portions or slats to carry the loose folds of the inner laps of the cloth and continually to push forward in an orderly manner the innermost laps so that they are progressively lessened in circumference.
C. O. C.

Web Feeding. John Waldron Corpn. and C. A. Dickhaut.
B.P. 639,728.

Apparatus for unrolling a web while feeding it for treatment, e.g. coating, with an efficient, inexpensive, and compact device for splicing two webs together immediately before the roll of the one being treated is expended.
C. O. C.

Suction Dryers for Cloth. Richmond Piece Dye Works Inc.   *B.P.* 639,786.

A stationary suction duct extends longitudinally in a perforated drying cylinder, its upper portion forming a longitudinal rectilinear narrow inlet slot close to the cylinder drying wall and underneath a point at which the cloth touches the cylinder. This gives very efficient high-speed suction.
C. O. C.

Homogeniser. Société Anonyme Française pour la Séparation, l'Émulsion et le Mélange (Procédés S.E.M.).
B.P. 640,564.

Mechanical Screen Printing. White, Child & Beney G.m.b.H.   *B.P.* 640,851.

A free-wheel mechanism is interposed in the motor drive for the fabric so as to make possible fine adjustment of the fabric without the need to move the main drive for the fabric.
C. O. C.

Separation of the Component Colours in the Reproduction of Multicolour Designs. N. W. Yelland.
B.P. 640,001.

Tubular Fabric Straightener. L. G. Blumenbaum, R. E. Langlois, and Draper Brothers Co.
U.S.P. 2,503,705.

A device is described for straightening tubular fabric as it leaves the hydroextractor for the drying machine.
C. O. C.

Tumbler-type Clothes Drier. Lovell Manufacturing Co.   *B.P.* 640,512.

Laundry Drier. J. R. Moore and Hamilton Manufacturing Co.
U.S.P. 2,506,516,
U.S.P. 2,506,517.

Applying Transfers to Hosiery. J. A. Ruth.
U.S.P. 2,501,539.

Ironing Machine for Leather or the like. Harrold Slocomb Machine Co. Ltd.   *B.P.* 640,042.

Removing Oil from Carded Webs, Batts, or Thin or Knitted Fabrics. G. H. Wood, C. S. Francis, and Felters Co. Inc. (VII, p. 565.)

Use of the Stroboscope on Printing Machines. B. Richter. (IX, p. 566.)

II— WATER AND EFFLUENTS

PATENT

Anti-foaming Agents. E. G. Parry and I.C.I. Ltd.
B.P. 640,464.

Conversion of the estolides of hydroxy fatty acids of $>$ 6 C into their ester–ethers with ethylene glycol and/or polyethylene glycol yields extremely efficient anti-foaming agents. Addition of 0·1–1·0 p.p.m. to a boiler water liable to foam and prime prevents any trouble in that direction.
C. O. C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Application of the Law of Mass Action to Micelle Formation in Colloidal Electrolyte Solutions. H. Lange. *Kolloid-Z.*, 117, 48–51 (April 1950).

The activity coefficients of the micelles are found to exert practically no influence on the critical concentration C_c for micelle formation. In consequence, data on the lowering of C_c by salt addition afford no conclusions on the activity coefficients of the micelles. The discovery by Corrin and Harkins (*J. Amer. Chem. Soc.*, 69, 683 (1947)) that log C_c is a linearly decreasing function of the logarithm of the total ionic concentration is explained, together with expected deviations, by application of the law of mass action to the activity coefficients. Other theoretical implications are critically examined.
H. H. H.

Kinetics of Long Chain Quaternary Salt Formation. S. K. Mukherjee and S. R. Palit. *J. Indian Chem. Soc.*, 27, 175–178 (April 1950).

The rate of formation of quaternary salts by the reaction between an alkyl halide and a tertiary amine has been measured by direct potentiometric titration of the disappearing base in non-aqueous medium. The reaction for long-chain quaternary salt formation is bimolecular and of speed of the same order as that for lower halides under similar conditions. The solvent effect is also found to be similar to the previous data for the lower halides. The compounds formed, e.g. cetylpyridinium chloride, are of great technical importance.
H. H. H.

Structure of Aqueous Solutions of Carboxymethyl Celluloses. G. Dürig and A. Banderet. *Helv. Chim. Acta*, 33, 1106–1118 (June 1950).

The very different rheological behaviour of two carboxymethyl celluloses, which possess almost the same molecular characteristics, is explained by the fact that they contain very different proportions of a fraction which is insoluble but swells strongly in water. This fraction is partly crystallised, and still retains in some degree the plant structure of the original cellulose. The micellar structure therefore characterises the carboxymethyl celluloses rather than their molecular size. In solutions of these compounds there exists a double association of molecules, the one amorphous and forming spontaneously owing to the ionised groups, the other crystalline and stable but not of spontaneous formation.
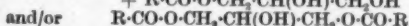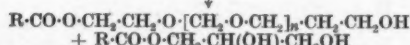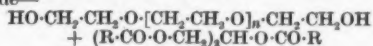H. H. H.

Studies on Foams. II— Foam Formation and Volume Contraction of Liquid Mixtures. M. Nakagaki. *Bull. Chem. Soc. Japan*, 22, (1), 21–24 (1949).

Foaminess and foam duration are tested in ternary mixtures of methyl alcohol, ethyl alcohol, and water, and for some binary systems. It is found that the volume contraction is closely connected with foaming properties, and this is interpreted in relation to the micelle formation of mixtures.
J. W. B.

Soromin SG (Hexaethylene Glycol Stearate) and some Dyes derived from 2-Furfuraldehyde. R. Oda. *Teijin Times* [Japan], 19, (4), 7–11 (1949): *Chem. Abs.*, 44, 5314 (25th June 1950).

Soromin SG is simply prepared by the ester-exchange reaction between polyethylene oxide and a natural glyceride—

$$HO \cdot CH_2 \cdot CH_2 \cdot O \cdot [CH_2 \cdot CH_2 \cdot O]_n \cdot CH_2 \cdot CH_2OH$$
$$+ (R \cdot CO \cdot O \cdot CH_2)_2 CH \cdot O \cdot CO \cdot R$$
$$\downarrow$$
$$R \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot [CH_2 \cdot O \cdot CH_2]_n \cdot CH_2 \cdot CH_2OH$$
$$+ R \cdot CO \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2OH$$

and/or $R \cdot CO \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot CO \cdot R$

($R \cdot COOH$ = a fatty acid).   2-Furfuraldehyde reacts with aromatic diazonium salts to form aryl-2-furfuraldehydes convertible to black dyes by mineral-acid treatment.
C. O. C.

PATENTS

Emulsifying Agents. J. K. Dixon, R. L. Morgan, and American Cyanamid Co.   U.S.P. 2,500,122.

Compounds of formula—

$R^1 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_2 \cdot [CH_2 \cdot CH_2 \cdot O]_x \cdot R^2]A$
(R^1 = sat. or unsat. C_{11-17} alkyl; R^2 = hydroxylic sat. C_{2-3} alkyl; x = 0 or a whole number; A = an anion), e.g. γ-stearamidopropyldimethyl - β - hydroxyethylammonium chloride, are emulsifying agents for resins, waxes, etc.
C. O. C.

Emulsifying Agents and Detergents. L. M. Jensca and J. Polasek.   B.P. 640,563.

The products obtained by condensing 3–10 mol. of urea with 1 mol. of hexamethylenetetramine at $>$ 100°c. have excellent emulsifying and detergent properties. C. O. C.

Anti-foaming Composition. Dow Corning Corpn. and C. C. Currie.   B.P. 639,673.

A mixture of a silica aerogel and a viscous, but flowable, methylsiloxane polymer, containing 1·75–2 C atoms per Si atom, can be drawn into threads which when broken have an elastic return similar to that of a rubber in a rubber cement; it is added to emulsion-type paints, non-aqueous varnishes, etc. to prevent foaming.   C. O. C.

Carrotting Solution. K. J. Hassan.   U.S.P. 2,500,678.

Use of an aqueous solution containing 1–15% of 2-nitro-2-methyl-1-propanol,   2-nitro-2-methyl-1:3-propanediol, 2-nitro-2-ethyl-1:3-propanediol,   or   trishydroxymethylnitromethane and 5–30% of nitric, hydrochloric, acetic, or formic acid results in a fur giving a strong and tight felt with no discoloration and excellent dyeing properties, good storability, and low wastage in felting and subsequent processing, and its action can be readily and rigidly controlled.   C. O. C.

Ungelatinised Starch Ethers from Polyfunctional Etherifying Agents. M. Konigsberg and National Starch Products Inc.   U.S.P. 2,500,950.

Inhibited starch, i.e. starch in which disintegration of the granules in water is retarded under conditions where starch granules ordinarily would swell and burst, which is resistant to alkali and does not cohere with untreated starch with which it may be mixed, is obtained by treating ungelatinised starch with an ether-forming agent, e.g. an aliphatic dihalide, so that the two reacting groups of ether-forming reagents react with two hydroxyl groups of the starch.   C. O. C.

Resinous Starching Composition. J. B. Beck.
U.S.P. 2,500,144.

A composition which gives a semi-permanent finish comprises by weight 70–74% water, 1–2% polyvinyl alcohol, 2–5% sodium carboxymethyl cellulose, and 20–26% of a 55–57% aqueous emulsion of polyvinyl acetate.   C. O. C.

Soap Substitute. H. F. Johnson.   B.P. 640,373.

A high fatty acid content is not necessary for cleansing efficiency, so that a mixture of stearin or stearic acid, sulphonated oil, sodium silicate, caustic potash, and water, the mixture having a fatty acid content of 5·5–19·0%, can readily replace normal soap; e.g. such a mixture having a fatty acid content of 14·375% is the equivalent in all laundry processes of ordinary soap of 65% fatty acid content.   C. O. C.

Water-soluble Urea Resins. W. L. Morgan and Arnold, Hoffman & Co. Inc.   U.S.P. 2,501,783.

Resins which may be kept for a long time in aqueous solution without hydrolysis are obtained by treating compounds of formula $X \cdot NH \cdot CO \cdot [NH \cdot R \cdot NH \cdot CO]_z \cdot NH \cdot X$ (X = H, alkyl groups of $<$ 6 C containing 1 or more OH or NH_2 groups, a polyaminoalkyl chain, or a simple amino radical; z = 0–3; R = $-[CH_2]_t \cdot [NH \cdot [CH_2]_t]_s-$; s = 0–5; t = 2–6, e.g. 2-methyl-2-ureido-1-propanol, with boric acid at 100–200°c.   C. O. C.

Water-repellent Finishing Compositions. J. Pikl and Du Pont.   U.S.P. 2,505,649.

Excellent initial water-repellency, good resistance to impact penetration, and excellent fastness to washing are obtained by impregnating textiles with an aqueous suspension of the precondensate of a hydroxymethylmelamine

and a hydroxymethylstearamide, or their lower alkyl ethers, and then baking. The precondensate is formed by heating the two components in alcoholic solution in presence of 0·4–0·5 mol. of HCl per mol. of hydroxymethylmelamine.   C. O. C.

**Water-repelling Organosilicon Compounds.** Société des Usines Chimiques Rhône-Poulenc. *B.P.* 640,162.

Incorporation in a polysiloxane liquid of at least 20% by weight of silicon dioxide, obtained by burning a silicon compound and rendered water-repellent by a coating of solid, insoluble polysiloxane, yields products having the consistency of grease, i.e. which do not flow at room temperature. They are useful for waterproofing paper, textiles, etc.   C. O. C.

Complex Salts of Stabilised Rosin Amine— Mildewproofing Agents. Hercules Powder Co. *B.P.* 640,402.

Treatment of not < 2 mol. of a stabilised rosin amine, e.g. dehydrogenated, disproportionated, or hydrogenated rosin amine, with 1 mol. of a complexogen metal salt, e.g. cupric acetate or zinc chloride, yields mildewproofing agents. Some of them are particularly useful in fireproofing compositions containing chlorinated paraffins, as they act as stabilisers for the latter.   C. O. C.

3 : 6-Epoxy-1 : 2 : 3 : 6-tetrahydrophthalonitriles— Mildewproofing Agents. D. T. Mowry and Monsanto Chemical Co.   *U.S.P.* 2,503,206.
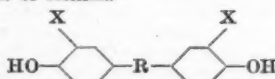
Compounds of formula—
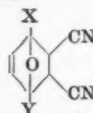
(X and Y = H and H, H and CH$_3$, H and –CH$_2$·O·CO·CH$_3$, or CH$_3$ and CH$_3$) are exceptionally effective mildewproofing agents for cotton textiles, jute, paper, etc.   C. O. C.

Bisphenols— Mildewproofing Agents. A. J. Dietzler, F. Bryner, and Dow Chemical Co.   *U.S.P.* 2,503,196.

Compounds of formula—

(X = H or Alk of 1–3 C; R = a cyclohexyl-substituted alkane structure; both benzene rings are attached to the same C atom of the alkane structure), e.g. 1-cyclohexyl-4:4-bis-m-isopropyl-p-hydroxyphenylpentane, have good mildewproofing properties.   C. O. C.

Stable Dry Preparations containing Alkali Sulphides. Ciba Ltd.   *B.P.* 639,998.

An alkali sulphide is mixed with starch or a water- or alkali-soluble cellulose ether in presence of water and under swelling conditions, the mixture being finally dried. If substances are present which may neutralise the reducing power of alkali sulphide, then a substantial excess of the latter is used. A sulphur dye or its leuco compound may be incorporated in the mixture.   C. O. C.

Dextran Base Wrinkle-drying Compositions. E. L. Luaces and New Wrinkle Inc.   *U.S.P.* 2,503,622   *U.S.P.* 2,503,623   *U.S.P.* 2,503,624.

A wrinkling oil is mixed with a solution of a dextran derivative, e.g. dextran benzyl ether or dextran acetate, in the ratio of 100 parts of oil to 10–50 parts of dextran derivative. Pigments previously blended with the wrinkling oil may be added to the composition, which may be brought to any desired viscosity with the usual varnish thinners. The compositions are applicable to paper, cloth, and similar flexible materials.   C. O. C.

Comparative Detergency of Surface-active Agents on Woollen Cloth. K. S. La Fleur. (VII, p. 564.)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Anomalous Thermal Expansion of the Short Intermolecular Bond in p-Nitroaniline. P. J. McKeown, A. R. Ubbelohde, and I. Woodward. *Nature*, **166**, 69–70 (8th July 1950).

A thermal study of the detailed crystal structure of p-nitroaniline has revealed an unusually short distance of approach (2·66 A.) between the oxygen atom of an NO$_2$ group of one molecule and one of the carbon atoms of the aromatic nucleus in a proximate molecule. This suggests special forces between these two atoms, the attraction of which appears to be intermediate between that in a covalent bond and that due solely to van der Waals forces, and may be electrostatic in origin. The possibilities of the observation are discussed.   H. H. H.

Mechanism of the Benzidine Rearrangement. E. D. Hughes and C. K. Ingold. *J.C.S.*, 1638–1639 (June 1950).

Recently, Hammond and Shine (*J. Amer. Chem. Soc.*, **72**, 220 (1950)) have adduced evidence that the rearranging entity is the bivalent cation $C_6H_5 \cdot \overset{+}{N}H_2 \cdot \overset{+}{N}H_2 \cdot C_6H_5$ (I), which appears to allow a solution of all the main difficulties. The original difficulty, which made Kidd, Hughes, and Ingold (*J.C.S.*, 954 (1933), 608 (1941)) refuse to contemplate fully formed $C_6H_5 \cdot \overset{+}{N}H_2 \cdot NH \cdot C_6H_5$ as the rearranging entity, viz. that of moving electrons from a positive to a neutral nitrogen atom, is overcome by making the second nitrogen positive; then, I has adjacent charges which can so weaken the N–N link that its electrons can functionally conjugate (or "hyperconjugate") with the aromatic π-electrons and thereby complete the internuclear conducting system. This would enable near-integral charges to be built up in the pp'-positions; and, even though the minimum separation of these positions would be about 4·2 A. in strainless I, this is not too great a distance for the establishment in II of a fairly strong electrostatic (or mainly electrostatic) bond; which, as the unlike charges come together and the like charges separate, would smoothly go over into a covalency in the product of the rearrangement.
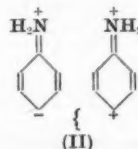
(II)   H. H. H.

Studies on Azo Dyes containing Chromium. V— Dyes from 4-Chloro-2-aminophenol-6-sulphonic Acid and 2:4-Dihydroxyquinoline. M. Hayashi, Y. Oshima, M. Kaizu, and T. Seo. *J. Soc. Org. Synthetic Chemistry Japan*, **7**, (3–4), 27–30 (1949): *Chem. Abs.*, **44**, 6130 (10th July 1950).

Potassium 4-chloro-2-aminophenol-6-sulphonate (76·8% purity) diazotised and coupled with 2:4-dihydroxyquinoline and then treated with chrome alum yields a deep purple–brown dye.   C. O. C.

Indoxyl Red. P. Seidel. *Chem. Ber.*, **83**, 20–26 (1950): *Chem. Abs.*, **44**, 5100–5102 (10th June 1950).

A detailed reinvestigation of the reactions of Indoxyl Red, αβ'-indolyl-β-indolone, with oxindole, NaHSO$_3$, alkali, KMnO$_4$, and NaNO$_2$, as a result of which 11 compounds, including some vat dyes and coloured sulphonic acids, have been prepared, their constitutions being given.   C. O. C.

Resonance and Colour in the Diazaphenanthrene Series. M. Colonna. *Boll. Sci. Facoltà Chim. ind. Bologna*, **7**, 55–57 (1949): *Chem. Abs.*, **44**, 5165 (25th June 1950).

Study of the relation between chemical constitution and colour has led to the proposal that to the auxochromophore groups of Brooker (*Advances in Nuclear Chemistry and Theoretical Organic Chemistry*, 1945) and of Ferguson (*Chem. Abs.*, **43**, 2923 (1949)) should be added the following new types—

Unionised Amidine
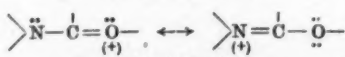
Ionised Amide   C. O. C.

Internal Dissociation, Colour, and Chemical Activity of Internal Complex and Cyclic Salts. V. I. Kuznetsov. *J. Gen. Chem. (U.S.S.R.)*, **20**, 807–815 (May 1950).

Effect of pH on the Colour of Solutions of Internal Complex and Cyclic Salts. Idem. *Ibid.*, **20**, 816–830 (May 1950).

A study is made of certain metal-containing organic compounds, e.g. the Ga, Al, Zr, and Ge derivatives of catechol, the Ga and Be derivatives of 3:4-dihydroxyazobenzene-4′-sulphonic acid, and the Cu and Al derivatives of 8-hydroxyquinoline, in which one metal atom is united to two neighbouring groups of the organic molecule. It is considered that in these compounds one of the linkages of the metal atom is generally subject to some degree of electrolytic dissociation, and that this internal dissociation is one of the factors determining the colour of the substance. In cases where the metal atom itself does not give rise to colour, the metal derivative is generally intermediate in colour between the dissociated and undissociated forms of the parent substance, so that in simple cases the colour in soln. may be closely matched by a soln. of the parent substance at the appropriate pH; a number of cases where this cannot be done are discussed. The internal dissociation affects the chemical reactivity of the substance in much the same way as dissociation affects the parent substance. Practical use may be made of this fact— thus the preparation of an azo dye from catechol in alkaline soln. is difficult owing to the strong tendency for catechol to oxidise under these conditions, but in presence of Al salts this difficulty may be avoided, for the degree of dissociation necessary for a sufficiently high coupling activity is attained in acid soln., where oxidation does not occur. The effect of pH on the colour of solutions of the metal compounds is considered. Internal dissociation diminishes with rise of pH, and the colour changes found are, in general, consistent with this. The considerations are extended to metals which give coloured ions, e.g. Fe, Cu, and Cr, and are applied, in particular, to the Fe derivatives of catechol and catecholdisulphonic acid. Some of these derivatives are here prepared for the first time, and it is shown that the existence of these new compounds is not readily interpreted on other views which have been advanced regarding the nature of such substances.   A. E. S.

Ultra-violet Absorption Spectra of Certain Heterocyclic Compounds in presence of Alkali. A. E. Lutsky. *J. Gen. Chem. (U.S.S.R.)*, **20**, 794–800 (May 1950).

The absorption spectra were determined in the 200–400 mμ. range of alcoholic solutions of rhodanine and *N*-phenylrhodanine in presence of sodium ethoxide. The data obtained are used in the interpretation of previous results on the spectra of the two photosensitising dyes 5-(3′-ethyl-2′:3′-dihydro-2′-benzthiazolidene)-rhodanine and 5-(3′-ethyl-2′:3′-dihydro-2′-benzthiazolidene-ethylidene)-rhodanine. The absorption curve of the first can be derived by superimposing the spectra of the two separate heterocyclic systems (benzthiazole and rhodanine) and adding a band characteristic of the system as a whole. The second dye, in which the heterocyclic nuclei are separated by a dimethin group, gives a very similar spectrum in which all the bands are uniformly displaced towards the long waves.   A. E. S.

Inhibitory Effect of Cyanine and Styryl Dyes upon Cholinesterase— I. E. Hase, Y. Mizuno, and M. Katayanagi. *Bull. Chem. Soc. Japan*, **22**, (6), 250–255 (1949).

Several cyanine and styryl dyes (e.g. 1:1′-diethyl-4:4′-monomethinquinocyanine iodide and *p*-dimethylamino-benzylidenequinaldine ethiodide) have a strong inhibitory action upon cholinesterases. For certain related styryl dyes, a relationship between chemical constitution and inhibitory effect on cholinesterase was observed.   H. H. H.

Effect of Foreign Molecules on the Absorption Spectra and Fluorescence of Magnesium Phthalocyanine and of Chlorophyll in Solution. V. B. Evstigneev, V. A. Gavrilova, and A. A. Krasnovsky. *Doklady Akad. Nauk S.S.S.R.*, **70**, 261–264 (11th Jan. 1950).

Previous work by these authors has shown that the intensity of the fluorescence of a soln. of chlorophyll in toluene falls when the pressure of air above the soln. is diminished, and rises again when the pressure is restored to normal. Simultaneously changes occur in the absorption spectrum. It was suggested that oxygen acts as an activator of fluorescence by addition to the central Mg. It is now shown that completely dry air has little influence on the absorption spectrum and fluorescence of a soln. of chlorophyll in dry toluene, and moisture must be regarded as the essential agent in the phenomenon previously observed. It is found that moisture in absence of oxygen causes a considerable increase in the fluorescence intensity, and that the introduction of oxygen then leads to a fall in intensity. It follows that, in presence of moisture, molecular oxygen quenches the fluorescence of chlorophyll in toluene soln. just as it does in solutions in polar solvents. Alcohols, pyridine, and many other substances act like water. It is considered that dry oxygen acts likewise, but that the effect is balanced, within the limits of experimental error, by its quenching action. Contrary to Livingston et al. (*J. Amer. Chem. Soc.*, **71**, 1542 (1949)), it is considered that the activator adds at the central Mg atom and not at the *cyclo*pentanone ring, and this is confirmed by experiments with phæophytin (which differs from chlorophyll only in the absence of Mg), phthalocyanine, and anhydrous magnesium phthalocyanine. The last does not contain a *cyclo*pentanone ring, but behaves like chlorophyll in toluene soln. On the other hand, phæophytin, although containing a *cyclo*pentanone ring, does not respond to fluorescence activators.   A. E. S.

Fluorescence of Magnesium Phthalocyanine and of Chlorophyll under Various Conditions— Action of Oxygen on the Fluorescence of Magnesium Phthalocyanine and of Chlorophyll in the Adsorbed State. V. F. Gachkovsky. *Doklady Akad. Nauk S.S.S.R.*, **70**, 51–54 (1st Jan. 1950).

Magnesium phthalocyanine was adsorbed on magnesium oxide from alcoholic soln. The preparation was dried, degassed at high temp. *in vacuo*, and cooled. It was exposed to radiation of λ = 366 mμ., and the fluorescence was observed through a red filter. Oxygen was slowly admitted, and the variation in fluorescence intensity observed (a correction was made for the fluorescence of the adsorbent). It was found that the first additions of oxygen, instead of producing the expected quenching effect, led to an increased intensity. At higher pressures of oxygen, quenching occurred. The maximum intensity attained depended on the temp. of the degassing operation, being high for high degassing temperatures. On reducing the pressure the intensity rose in a reversible manner as far as the maximum point, but then, on completing the evacuation, remained constant at this elevated value. The fluorescence spectrum of magnesium phthalocyanine in soln. is related to the absorption spectrum in mirror-image fashion. Adsorption on magnesium oxide leads to a displacement of both spectra towards the short waves. Chlorophyll was examined in a similar way and found to behave analogously. Three possible explanations are given. The first assumes adsorption of the pigments as dimers which dissociate on treatment with oxygen, which attacks the central Mg. The further action of oxygen is at the periphery of the molecule, and leads to quenching. The second assumes adsorption as monomer. Oxygen at low pressure is taken up preferentially by the Mg of the pigment, leading to the splitting of the latter from direct contact with the adsorbent. The third assumes that the adsorbed molecules fluoresce only after forming a complex with oxygen or with residual oxygen-containing solvent. These complexes are broken down during degassing to an extent which depends on the degassing temp. Each theory assumes that addition of oxygen occurs at the two unoccupied co-ordination places of the Mg. The experimental data are not sufficient to decide between these possibilities. In the light of these experiments, and in view of the non-applicability of the keto–enol tautomerism hypothesis to magnesium phthalocyanine, it is considered that the interpretation of the nature of the fluorescence of chlorophyll solutions recently given by Livingston et al. (*J. Amer. Chem. Soc.*, **71**, 1542 (1949)) is not very probable.   A. E. S.
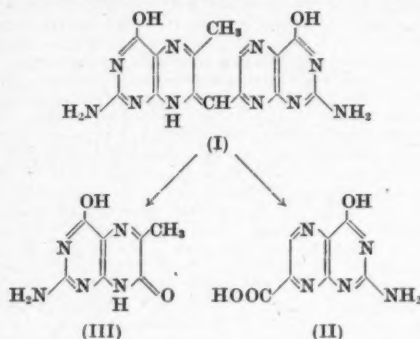
Azulenes. A. J. Haagen-Smit. *Fortschr. Chem. org. Naturstoffe*, **5**, 40–71 (1948): *Chem. Abs.*, **44**, 5793 (10th July 1950).

Review with many references.   C. O. C.

Constitution of Methylpteridine Red. P. Karrer, B. Nicolaus, and R. Schwyzer. *Helv. Chim. Acta*, **33**, 1233–1236 (Aug. 1950).

Ozonisation of methylpteridine red (I) in formic acid gives 2-amino-6-hydroxypteridine-9-carboxylic acid (II) and methyl*iso*xanthopterine (III), from which the structure (I) follows for the parent substance.

(I)

(III)   (II)

H. H. H.

Carotenoid Epoxides and Furanoid Oxides of Carotenoid Pigments. P. Karrer. *Fortshr. Chem. org. Naturstoffe*, **5**, 1–19 (1948): *Chem. Abs.*, **44**, 5793 (10th July 1950).

Review with many references.   C. O. C.

Syntheses in Carotenoid Chemistry since 1939. H. H. Inhoffen and F. Bohlmann. *Fortschr. chem. Forsch.*, **1**, 175–210 (1949): *Chem. Abs.*, **44**, 5849 (10th July 1950).

It is proposed to apply the term *carotenoids* to any substance containing part of the typical C skeleton from γ-carotene to any isoprene derivative containing 10 C. This would include the large number of synthetic materials important in synthesising the classic carotenoids. The various methods of synthesising carotenoids containing 10–40 C are reviewed. There are 65 references. C. O. C.

Gastropod Shell Pigment. A. Comfort. *Nature*, **166**, 194–195 (29th July 1950).

A subsidiary yellow pigment from the shell of *Haliotis cracherodii* Leach is examined spectrographically, and the zinc complex prepared. Although the absorption spectrum is not consonant with any of the commoner natural pyrroles, the behaviour of the zinc complex is suggestive of a pyrrolic and not of an indigoid material. J. W. B.

The Phenazine Series. VIII— Constitution of the Pigment of *Chromobacterium iodinum*. G. R. Clemo and A. F. Daglish. *J.C.S.*, 1481–1485 (June); xiv (July 1950).

The syntheses of 1:2-, 1:6-, and 1:9-dimethoxyphenazines are described and also the demethylation of the 1:6 and 1:9 isomerides. The 1:6-dimethoxyphenazine was found to be identical with that derived from the pigment of *Chromobacterium iodinum* (iodinin), which must therefore be the 1:6-dihydroxyphenazine di-N-oxide—

H. H. H.
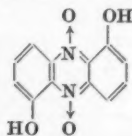
Absorption of Gelatin–Dye Phosphors. P. Frohlich and P. Szor. *Acta Univ. Szeged, Chem. et Phys.*, **2**, 61–67 (1948): *Chem. Abs.*, **44**, 5712 (10th July 1950).

The absorption spectrum of sodium fluorescein shows two maxima at 480 and 465 mμ. The spectral distribution and form of absorption curves of its gelatin–dye phosphor are the same as in aqueous solution; thus the absorbing ions or ion groups are unchanged. The absorption coefficients of all gelatin–dye solutions are functions of the coefficients. The thickness of plates and concentration have certain effects. The reflection constant seems to be independent of λ.   C. O. C.

Phosphorescence of Organic Materials in Solid Solutions. T. Förster. *Naturwissenschaften*, **36**, 240–245 (1949): *Chem. Abs.*, **44**, 5694 (10th July 1950).

A review with references.   C. O. C.

Orientation of Molecules in Gelatin Dyes as the Cause of Pre-excitation. P. Frohlich and L.Szalay. *Acta Univ. Szeged, Chem. et Phys.*, **2**, 111–118 (1948): *Chem. Abs.*, **44**, 5712 (10th July 1950).

Experiments with rigid gelatin solutions of Rhoduline Orange N proved that if the planes of polarisation of pre-exciting and that of measuring light were perpendicular, the effect was smaller both with positive and negative pre-excitations. Phenomena of positive and negative pre-excitation are explained by assuming orientation of the molecules. The rate of orientation increases with diminishing concentration. Both normal and abnormal orientation can occur in the same dye under different conditions.   C. O. C.

Acetylene Black, an Industrial Example of a Turbulent Flame Reaction. J. Wotschke and K. Paasch. *Schweiz. Arch. angew. Wiss. Tech.*, **15**, (6), 176–187 (1949): *Chem. Abs.*, **44**, 6105 (10th July 1950).

A detailed discussion of the physicochemical principles of the production of acetylene black. Laboratory, pilot plant, and industrial methods for carrying out the reaction are described.   C. O. C.

Carbon Blacks formed by Decomposition of Mixtures of Acetylene with a Hydrocarbon or other Gas at Elevated Pressures. G. W. Jones, R. E. Kennedy, I. Spolan, and G. S. Scott. *U.S. Bur. Mines, Rept. Invest. No.* 4695, 9 pp. (1950): *Chem. Abs.*, **44**, 6104 (10th July 1950).

Definite mixtures of the endothermic acetylene and various exothermic gases (CH_4, natural gas, N_2, He, CO_2, C_2H_6, C_3H_8, and C_4H_{10}) were exploded in a high-pressure bomb. The carbon blacks produced had a chain-like structure comparable with that of acetylene blacks. Not < 90% of the C in the test mixtures was converted to carbon black.   C. O. C.

History of Artists' Pigments. H. J. Plenderleith. *Science Progress*, **38**, 246–256 (1950): *Chem. Abs.*, **44**, 5608 (25th June 1950).

A concise account of the pigments used by Egyptian, Roman, mediæval, and modern artists.   C. O. C.

PATENTS

N-2-Furoyl Derivatives of Aminonaphthols— Intermediates for Azo Dyes. H. W. Grimmel, A. F. Strobel, and General Aniline & Film Corpn.
B.P. 639,697.

The acid halides of 2-furoic acid and its derivatives react with aminonaphthols to produce amides. Azo dyes can be made by coupling these with diazo compounds, and they may also be used as couplers in the diazotype process and in colour photography. Thus 2-furoyl chloride reacts at 35°c. with 1-amino-7-naphthol suspended in aqueous sodium carbonate to give the corresponding amide. E. S.

Diaminodiphenylureas. Ciba Ltd.   B.P. 639,021.

Diaminodiphenylureas, which may carry nuclear substi. uents, are made by condensing the corresponding *m*- or *p* phenylenediamines with urea in aqueous medium at not < 100°c. Thus an aqueous solution of 2 mol. of *p*-phenylenediamine is boiled with 1 mol. of urea to yield 4:4′-diaminodiphenylurea. When *m*-diamines are used, the reaction is best carried out in presence of sulphuric acid.   E. S.

2-*p*-Aminophenyl-2 : 1 : 3-benzotriazoles — Intermediates for Azoic Dyes. R. P. Parker, J. Seruto, and American Cyanamid Co.
U.S.P. 2,501,188.

Compounds of formula—
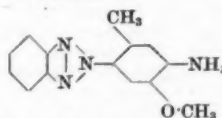
e.g. 2-(2′-methyl-5′-methoxy-4-aminophenyl)-2:1:3-benzo-triazole, are readily diazotised to stable diazo compounds

of very strong coupling activity, which yield maroons to violets of excellent brilliance, marked fastness to washing and strong alkalis, and satisfactory fastness to light when coupled with arylides of hydroxynaphthoic acids.

C. O. C.

Urethanes of *N*-substituted J Acids as Colour Formers. General Aniline & Film Corpn. and V. Tulagin. *B.P.* 640,109.

The urethanes of *N*-aliphatic or *N*-aromatic J acids are soluble in water, aqueous alkalis, and alcohol, of good stability when incorporated in photographic emulsions, and unaffected by ferricyanide bleaching solutions used in colour photography, so that dyes prepared from them are not altered in hue during processing.   C. O. C.

Colour Formers for Azine Dyes. General Aniline & Film Corpn. *B.P.* 640,122.

Compounds of formula—
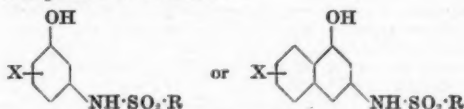
(R = aliphatic or aromatic radical, e.g. alkylphenyl or acylaminophenyl (e.g. stearoylaminophenyl); X = H, Alk, an aromatic radical, or SO_2H) yield azine dyes with the oxidation products of primary aromatic amines. The reaction involves two conversions, which may take place simultaneously or in observable sequence. The first reaction is the formation of a quinoneimine dye, and the second, ring closure of the quinoneimine to the desired azine.   C. O. C.

Diazotype Compositions containing Ethylene Oxide Derivatives of Light-sensitive Diazo Compounds. General Aniline & Film Corpn., W. H. von Glahn, L. N. Stanley, and G. T. Parker. *B.P.* 640,041.

Bright dark prints of great permanency and fastness to washing are obtained by using as the light-sensitive material a diazo derivative of a compound of formula—

$$NH_2 \cdot Ar \cdot NR \cdot [CH_2 \cdot CH_2 \cdot O]_m \cdot H \text{ or}$$
$$NH_2 \cdot Ar \cdot N([CH_2 \cdot CH_2 \cdot O]_n \cdot H)_2$$
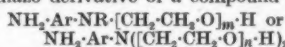
($m > 1$, $n =$ a whole number, the two n's being the same or different; R = alkyl, hydroxyalkyl, alkoxyalkyl, aryl, aralkyl, or acyl; Ar = an aromatic radical (linked *ortho* or *para* to the two N's) which contains no alkyl substituent of > 3 C but which may contain other substituents), e.g. $p \cdot NH_2 \cdot C_6H_4 \cdot N(CH_2 \cdot CH_2OH)_2$.   C. O. C.

Intermediates for Cyanine Dyes. General Aniline & Film Corpn. and A. W. Anish. *B.P.* 639,758.

Intermediates for cyanine dyes are obtained by (1) treating a quaternary salt of a nitrogenous heterocyclic base containing a reactive methyl group in the *a*-position to the heterocyclic N with phenyl *iso*cyanate or phenyl *iso*selenocyanate in presence of an organic base and alcohol, and (2) alkylating the resulting compound with an alkyl or aralkyl ester.   C. O. C.

Benziminazole Colour Formers. W. C. Craig and General Aniline & Film Corpn. *U.S.P.* 2,500,487.

Compounds of formula—
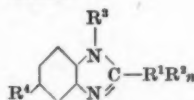
(R^1 = subst. or unsubst. phenyl; R^2 = $-NH \cdot CO \cdot CH_2 \cdot A$ (A = alkyloyl, aroyl, CN, or $COOC_2H_5$); R^3 = an alkyl chain of > 9 C; R^4 = a water-solubilising group; $n =$ 1 or 2) yield yellow dyes with developers of the *p*-phenylenediamine type and are more soluble than the ketomethylene compounds usually used for this purpose.

C. O. C.

Diketone Azo Components for Diazo Sulphonate Light-sensitive Elements. J. M. Straley and General Aniline & Film Corpn. *U.S.P.* 2,500,099.

5-Alkyl- and 5:5-dialkyl-1:3-*cyclo*hexanediones have good resistance to precoupling, give good reds with diazo compounds, and may be used in aqueous or non-aqueous coatings.   C. O. C.

Metallisable Monoazo Dyes. K. F. Conrad and Allied Chemical & Dye Corpn. *U.S.P.* 2,499,133.

Monoazo dyes which may be metallised in substance or on the fibre are made by diazotising a sulphonamide of *o*-aminophenol and coupling with a 1-acylamino-7-naphthol. Thus the monoazo compound 2-aminophenol 4 - sulphonamide $\rightarrow$ 1 - acetylamino - 7 - naphthol dyes wool violet–blue from an acid bath, and yields blue–blacks when applied by the chrome mordant, metachrome, or afterchrome process.   E. S.

Brown Azoic Dyes. J. H. Trepagnier and Du Pont. *U.S.P.* 2,499,800.

Brown azoic dyeings are produced by coupling a 2-hydroxy-7-benzo-(c)-carbazole—
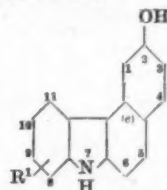
(R^1 = H, alkyl of < 6 C, phenyl, Cl, or F) with a diazotised *p*-nitroaniline—

(R^2 = H, alkyl of < 6 C, alkoxy of < 6 C, Cl, or F). These coupling components are simpler than the arylamides of heterocyclic *o*-hydroxycarboxylic acids commonly used for azoic browns, and have the advantages of higher solubility and lower substantivity for the fibre. Thus by padding cotton with a solution of the sodium salt of 2-hydroxy-7-benzo-(c)-carbazole, developing with diazotised *p*-nitroaniline, and soaping, chocolate browns are produced.

E. S.

Anthraquinone— Improved Friedel–Crafts Process. G. M. Smyth, A. E. Moran, and American Cyanamid Co. *U.S.P.* 2,496,894.

In preparing anthraquinone by first condensing phthalic anhydride with benzene in presence of anhydrous aluminium chloride, the two stages (i) decomposition of the resulting aluminium chloride complex and (ii) ring closure of the *o*-benzoylbenzoic acid are carried out without isolating the intermediate products by adding 5–20% oleum directly to the product of the Friedel–Crafts reaction, at 105–150°C., contained if necessary in the same reaction vessel, e.g. a ball mill. The amount of oleum used is 0·9–1·3 parts per 1 part of Friedel–Crafts product.

R. K. F.

Acylated 1-Amino-5-hydroxyanthraquinones—Dyes for Cellulose Esters, Superpolyamides, and Polyvinyl Compounds. Ciba Ltd. *B.P.* 639,250.

Yellow dyes for cellulose acetate and nylon are made by acylating a 1-amino-5-hydroxyanthraquinone with an aliphatic carboxylic acid of > 2 C, or a functional derivative thereof. Thus, 1-amino-5-hydroxyanthraquinone is treated at 120°C. for 30 min. with propionyl chloride in *o*-dichlorobenzene containing dimethylaniline. The dye separates on adding methanol.   R. K. F.

Acylated 1-Amino-8-hydroxyanthraquinones — Dyes for Cellulose Esters, Superpolyamides, and Polyvinyl Compounds. Ciba Ltd. *B.P.* 639,223.

Yellow dyes for cellulose acetate and nylon are made by acylating a 1-amino-8-hydroxyanthraquinone free from solubilising groups with an aliphatic carboxylic acid or a functional derivative thereof. Thus, 1-amino-8-hydroxyanthraquinone is treated at 60°C. for 1 hr. with acetyl chloride in pyridine. The dye is separated by adding methanol.   R. K. F.

1 - Hydroxy - 2(or 3) - cyano - 4 - alkyl(or aryl)amino-anthraquinones— Dyes for Cellulose Esters. British Celanese Ltd. *B.P.* 639,587.

Blue dyes for cellulose acetate, fast to gas fumes, are prepared by treating a 1-amino-2(or 3)-cyano-4-alkyl(or aryl)aminoanthraquinone at 140–150°C. in aqueous medium of pH 8–9, when the NH_2 group is replaced by OH. Thus, 1-amino-2-cyano-4-butylaminoanthraquinone is heated in

an autoclave at 145°C. for 2 hr. with dil. NaHCO₃ solution containing in suspension a small amount of filter-aid material. The product on cooling separates in pellets, which are freed from the filter-aid by pouring the reaction mixture through an 80-mesh sieve.   R. K. F.

Aminoanthraquinone – Sulphonamides — Dyes for Animal and Superpolyamide Fibres. C. G. Vogt and General Aniline & Film Corpn.   B.P. 639,660.

Blue dyes for wool, silk, and nylon are made by condensing sodium 1-amino-4-bromoanthraquinone-2-sulphonate with an aminobenzoic acid containing a sulphonamide group. Thus, the dye—
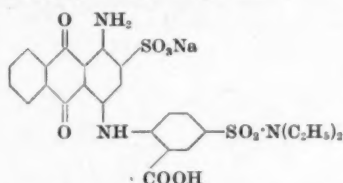
s made by heating 5-NN-diethylsulphamylanthranilic acid and sodium 1-amino-4-bromoanthraquinone-2-sulphonate at 95°C. for 90 min. in water containing sodium acetate and cuprous chloride.

E. E. Renfrew and General Aniline & Film Corpn.   B.P. 639,662.

The neutral-dyeing properties of the dyes of the preceding patent are improved by esterifying the carboxyl group(s) by refluxing with a mixture of an aliphatic alcohol and sulphuric acid.   R. K. F.

Aminoanthraquinone β-Thioethers— Dyes for Cellulose Esters and Ethers. Celanese Corpn. of America.   B.P. 639,266.

Red dyes for cellulose esters, of good fastness to gas fumes, are made by etherifying a 1-amino- or 1-amino-4-hydroxy-2(or 3)-mercaptoanthraquinone. Alternatively, a derivative in which halogen replaces the thiol group is treated with an alcohol and sulphur. Thus, 1-amino-2-mercapto-4-hydroxyanthraquinone is heated at 80°C. for 4 hr. in alkaline solution with dimethyl sulphate.   R. K. F.

Benzoylaminoanthraquinones containing a Sulphonamide Group— Vat Dyes. Ciba Ltd.   B.P. 636,691.

Pink vat dyes of general formula—
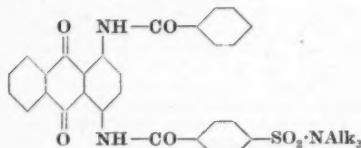
are prepared by treating a 1-benzoylamino-4-aminoanthraquinone with a p-NN-dialkylsulphamylbenzoic acid (or its acid chloride), or alternatively a 1-amino-4-p-(NN-dialkylsulphamyl)benzoylaminoanthraquinone with a substituted benzoic acid. Thus, p-NN-dimethylsulphamylbenzoic acid and thionyl chloride are stirred at 120–130°C. for 2 hr. in nitrobenzene. 1-Amino-4-p-chlorobenzoylaminoanthraquinone is then added, and stirring continued for a further 150 min. The resulting dye separates on cooling.   R. K. F.

Thiophanthraquinone. V. Weinmayr and Du Pont.   U.S.P. 2,497,334.

Thiophanthraquinone—
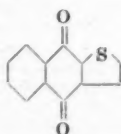
is prepared by condensing thiophen with phthalic anhydride in nitrobenzene in presence of anhydrous aluminium chloride at 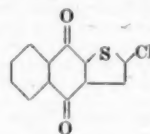30–70°C. The resulting o-2-thienoyl-benzoic acid is cyclised without being isolated by adding more aluminium chloride and heating at 120–125°C. After separating, the crude thiophanthraquinone is purified by dissolving in aqueous sodium sulphide and reprecipitating by blowing air through the solution.   R. K. F.

2-Chlorothiophanthraquinone. H. R. Lee, V. Weinmayr, and Du Pont.   U.S.P. 2,497,312.

2-Chlorothiophanthraquinone—

is prepared by condensing α-chlorothiophen with phthalic anhydride in presence of anhydrous aluminium chloride in nitrobenzene at 80–90°C. Ring closure of the resulting o-(5-chloro-2-thienoyl)benzoic acid is effected without isolation by adding more aluminium chloride and raising the temperature to 120–125°C.   R. K. F.

Alkylated Dihydroxybenzanthrones — Green Vat Dyes. Cincinnati Chemical Works Inc. and Ciba Ltd.   B.P. 636,008.

Improved green vat dyes are obtained by heating a dioxo-dibenzanthrone or -isodibenzanthrone in an inert high-boiling solvent with an alkylating agent, an acid-binding agent, and a substance capable of reducing the dioxo compound, e.g. a tetrahydronaphthalene, a phenol, or a hydrazine. Thus, dioxodibenzanthrone is heated at 170–180°C. in trichlorobenzene with dimethyl sulphate, sodium carbonate, and phenol.   R. K. F.

Phthaloylpyrene Derivatives— Vat Dyes. Ciba Ltd.   B.P. 636,205.

Olive to grey vat dyes are made by carbazolising a 3:4-phthaloylpyrene containing in the 3′ and 6′ positions –NH·R groups (R = similar or different vattable residues). Thus the compound—
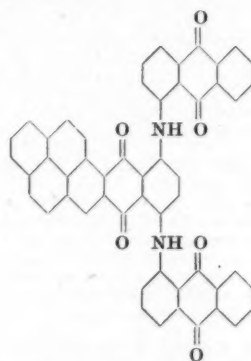
made by first condensing pyrene with 3:6-dichlorophthalic anhydride and eliminating water by treating with phosphorus pentoxide, and then refluxing with α-aminoanthraquinone and sodium carbonate in nitrobenzene, is heated at 121–123°C. in a mixture of aluminium chloride and dry pyridine. The resulting dye is separated by pouring into water.   R. K. F.

isoThiouronium Derivatives — Dyes for Textile Printing. C. Wood and I.C.I. Ltd.   B.P. 639,487.

Water-soluble dyes sufficiently stable in alkaline media to be used in conjunction with stabilised diazo compound–coupling component mixtures are made by treating one of the dyes containing a tetramethylisothiouronium group described in B.P. 576,270 and 587,636 (J.S.D.C., **62**, 327 (1946); **63**, 304 (1947)) with an alkylating agent. Thus, the isothiouronium salt derived from copper trischloromethylphthalocyanine and tetramethylthiourea is heated at 100–110°C. for 10 min. with dimethyl sulphate. The resulting blue dye is separated by adding acetone.   R. K. F.

Green Pigment. M. Scalera, R. E. Brouillard, and American Cyanamid Co. *U.S.P.* 2,505,744.

Products of outstanding brilliance and colour stability are obtained by blending blue or greenish-blue phthalocyanine pigments with yellow α-aroylaminoanthraquinone pigments. Their strength is greater than that calculable from the individual pigment components themselves. C. O. C.

Azanol Dyes. A. W. Anish, L. C. Hensley, and General Aniline & Film Corpn. *U.S.P.* 2,500,111.

Dyes of formula—

$$R \cdot O \cdot C == C \cdot [CH]_n : N \cdot X \cdot N : [CH]_n \cdot C == C \cdot O \cdot R$$
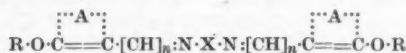
(A = atoms to complete a 5- or 6-membered heterocyclic nucleus; $n = 1$ or 3; $N \cdot X \cdot N$ = radical of hydrazine or a primary diamine containing < 15 C; R = H or a heavy metal), obtained by heating an alcoholic solution of hydrazine or a diamine with a 5- or 6-membered heterocyclic derivative of a barbituric acid or the like having a reactive acetanilide group linked to a C atom of a mono- or poly-methin chain of < 4 C adjacent to a keto group, are photographic sensitisers and filter and antihalation dyes. C. O. C.

Dianil Dyes. G. W. Sawdey and Eastman Kodak Co. *U.S.P.* 2,500,045.

Dyes of formula—

$$R^3 \cdot NR^2 \cdot R^1 \cdot N : CH \longrightarrow CH : N \cdot R^1 \cdot NR^2 \cdot R^3$$
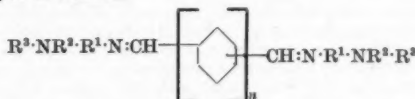
($n = 0$ or 1, $R^1 = p$-phenylene, R^2 and R^3 each = H or Alk) are obtained by treating a p-phenylenediamine with a dialdehyde; e.g.—

$$(C_2H_5)_2N \underset{CH_3}{\longrightarrow} N = CH \longrightarrow CH = N \underset{CH_3}{\longrightarrow} N(C_2H_5)_2$$

from 2-amino-5-diethylaminotoluene and terephthalaldehyde. C. O. C.

**Hemicyanine Dyes.** Gevaert Photo-Producten N.V. *B.P.* 640,094.

Simple hemicyanine dyes are obtained by treating suitable intermediates, e.g. cyclammonium salts having a vinyl group linking the C α or γ to the N with a reactive group, with excess of a primary aromatic amine or diamine. No symmetrical double hemicyanine dye is produced. Symmetrical or unsymmetrical double hemicyanine dyes are obtained by condensing the above simple hemicyanine dyes with more of the above intermediates. C. O. C.

Cyanine Dyes. F. P. Doyle and Ilford Ltd. *B.P.* 640,127.

Cyanine dyes are produced by condensing a compound of formula $Y \cdot C(CHO) : CH \cdot X$ ($Y = CN$ or $COOR$; $X = SR$ or NHR; R = Alk of 1–4 C or Ar of 6–10 C) with a heterocyclic compound containing a reactive methylene group; e.g. bis-2-(3-ethylbenzthiazole)-γ-carbethoxypentamethincyanine iodide from α-carbethoxymalondialdehyde monoanil and 2-methylbenzthiazole ethiodide. C. O. C.

N-Aryloxy-, N-Arylthio- and N-Arylseleno-alkyl Cyanine Dyes. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,504,615.

*meso*Cyanine and rhodacyanine dyes containing the following heterocyclic nucleus—

$$R - A - [CH_2]_m - N --- C =$$
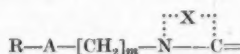
(R = Ar of the benzene or naphthalene series; A = O, S, or Se; $m = 2$ or 3; X = non-metallic atoms to complete a heterocyclic nucleus; the C in the nucleus is α or γ to the N) can be prepared by condensing a suitable cyclammonium quaternary salt in presence of a base with an appropriate ketomethylene compound. C. O. C.

Dye Salt Intermediates for Heterocyclic Nitrogenous Cyanine or p-Dialkylaminostyryl Dyes having a New Group attached to the Nitrogen Atom. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,504,616.

Introduction of one or two methylene groups between a p-toluenesulphonate group and a nitrogenous heterocyclic system yields compounds which when used as alkylating or quaternising agents for basic nitrogenous heterocyclic dye intermediates yield dye salt intermediates which undergo the usual reactions for preparing cyanine dyes.

U.S.P. 2,504,617.

Styryl dyes are formed by condensing the above dye salt intermediates with p-dialkylamino aromatic aldehydes. C. O. C.

Trinuclear Cyanine Dyes. A. W. Anish, C. A. Clark, and General Aniline & Film Corpn. *U.S.P.* 2,500,112.

Trinuclear cyanine dye salts in which the central nucleus, diazole or triazole, is linked to the other two nuclei by both a methin and an azamethin chain are readily soluble in water, non-migrating, excellent sensitisers, and unaffected by the presence of colour components.

C. O. C.

Trinuclear Cyanine Dyes. T. R. Thompson and General Aniline & Film Corpn. *U.S.P.* 2,504,468.

Dyes of formula—

$$N \cdot (CH : CH)_m \cdot C : [CH \cdot CR^1]_n = C - S$$
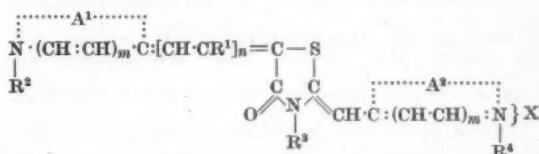
(A¹ and A² = same or different heterocyclic nitrogenous nuclei; $m = 0$ or 1; $n = 0$–3; R^1 = H, Alk, or phenyl, but only Alk or phenyl when $n = 1$; R^2 and R^4 = same or different, subst. or unsubst. Alk or aralkyl; R^3 = Alk, allyl, Ar, or aralkyl; X = an acid radical) are obtained in excellent yield and readily purifiable form by treating a cyclammonium quaternary salt, containing a particular reactive group of the type used in cyanine dye syntheses, with a thiazolone cyanine dye in a suitable solvent at room temperature for 1 hr., or in a few min. by heating the mixture. C. O. C.

Cadmium Red. J. J. O'Brien and Glidden Co. *U.S.P.* 2,504,147.

The crude cadmium red greencake is washed free of water-soluble compounds, then mixed with 0·5–10·0% of hydrazine sulphate, or an alkali-metal sulphite, acid sulphite, hyposulphite, sulphate, or thiosulphate, and finally calcined at 350–700°c. This yields cleaner, brighter red pigments free from CdO and with less variation between batches. C. O. C.

γ-Ferric Oxide Hydrate and γ-Ferric Oxide. Columbian Carbon Co. and J. Martin. *B.P.* 640,438.

γ-Ferric oxide hydrate is obtained by precipitating a solution of ferrous sulphate with an alkali or alkaline-earth metal hydroxide at 150–200°F., maintaining that temperature until the slurry is thin, diluting and cooling the slurry, and finally oxidising it until the precipitate is a clean orange–yellow. Heating the γ-ferric oxide hydrate at 450–500°F. produces the brown γ-ferric oxide. C. O. C.

Magnesium Ferrite Pigment. C. D. Downs, J. Martin, and Columbian Carbon Co. *U.S.P.* 2,502,130.

Addition of a suitable catalyst, e.g. 0·2% of MgCl₂, to a stoichiometric mixture of iron oxide and magnesium oxide or carbonate followed by heating, e.g. for 30 min. at 950°c., produces pigments whose colour is not changed when heated to > 200°c. C. O. C.

Titanium Dioxide. H. H. Schaumann and Du Pont. *U.S.P.* 2,502,347.

Finely divided rutile pigment free from gritty particles is obtained by oxidising titanium halide vapour in presence of an oxide of nitrogen. C. O. C.

Titanium Dioxide. C. A. Tanner and American Cyanamid Co.   *U.S.P.* 2,503,692.

Amorphous hydrous titanium dioxide is produced by hydrolysing aqueous titanium sulphate (12–16% TiO_2 content) in presence of a little of an alkali-metal titanate. This titanate is prepared by boiling an aqueous slurry of purified titanium sulphate hydrolysate in presence of an alkali-metal hydroxide for 1–6 hr., filtering the mixture, and washing excess alkali from the residue. The hydrous titanium dioxide can be calcined to either the anatase or the rutile form.   C. O. C.

U.S.P. 2,505,344.

The seed prepared from titanium phosphate is equally and often more active than hitherto known seeds in converting anatase TiO_2 into the rutile form.   C. O. C.

Zinc and/or Cadmium Sulphide and Selenosulphide Pigments. J. J. O'Brien and Glidden Co.

U.S.P. 2,500,958.

Extended or unextended zinc and/or cadmium sulphide or selenosulphide pigments of improved tinting strength, colour, and texture are obtained by precipitating them from solutions of zinc and/or cadmium salts by means of a solution of an alkaline-earth metal sulphide which has been cooled so as to precipitate alkaline-earth metal hydroxide, part or the whole of which has been removed before adding the liquor to the zinc and/or cadmium salt solution.

C. O. C.

Anti-foaming Agents. E. G. Parry and I.C.I. Ltd. (II, p. 555.)

Soromin SG (Hexaethylene Glycol Stearate) and some Dyes derived from 2-Furfuraldehyde. R. Oda. (III, p. 555.)

Stable Dry Preparations containing Alkali Sulphides. Ciba Ltd. (III, p. 556.)

Diazotype Printing Materials. General Aniline & Film Corpn. and S. C. Slifkin. (IX, p. 566.)

V—PAINTS; ENAMELS; INKS

PATENTS

Flushing of Pigments. Lewis Berger & Sons Ltd.

B.P. 640,404.

*cyclo*Hexylamine or an *N*-substituted methyl, ethyl, phenyl, or *cyclo*hexyl derivative, preferably in the form of its soap with a fatty or resin acid, is an extremely efficient flushing agent for use with both inorganic and organic pigments.   C. O. C.

Emulsion Paints. Lewis Berger & Sons Ltd., D. H. Hewitt, and L. A. Paxon.   *B.P.* 640,502.

An emulsion paint, which gives a glossy film, is readily thinned with water to give an easily brushing product, and gives a waterproof film on porous surfaces, is obtained by forming an aqueous emulsion of a pigment–air-drying oil dispersion with the aid of an emulsifying agent and a naturally occurring organic protective colloid, the amount of the latter being 4–14% by weight of the disperse phase. The disperse phase contains 20–70% by weight of pigment and, if necessary to reduce the viscosity, a volatile solvent.

C. O. C.

VI—FIBRES; YARNS; FABRICS

Studies in Detergency. VIII— Electron-microscopic Observations of Fibre Surfaces. W. Kling and H. Mahl. *Melliand Textilber.*, 31, 407–413 (June 1950).

In connection with an extensive investigation on detergency it was decided to make observations of the surface of fibres using the electron microscope. This paper, which is illustrated by many photomicrographs, describes the preliminary results obtained with clean fibres of cotton, flax, wool, silk, viscose and acetate rayons, and nylon. With cotton the fibrillæ of the secondary wall were visible through the cuticle and primary wall. The presence of a thin outer skin, which fairly readily flaked off, was observed on nylon.   F. A.

Electrokinetic Properties of Cellulose Fibres. I— Stream Potential and Electro-osmosis. D. A. I. Goring and S. G. Mason. *Canadian J. Res.*, B 28, 307–322 (June 1950).

Stream potential, electro-osmotic, and permeability measurements have been made on cotton pads in the

presence of distilled water. Several sources of irreproducibility have been eliminated from the usual experimental methods of measuring the ζ-potential, the importance of uniform packing of the pad being stressed. The Briggs method (*J. Phys. Chem.*, 32, 641 (1928)) of evaluating the "pore factor" by electrical conductivity measurements was found to be invalid, and an alternative method is proposed, based on an assumed value for the pore orientation factor and an indirectly measured value of the swollen specific volume of the fibres. When pads of different concentrations were used, the stream potential, electro-osmotic, and permeability functions were found to vary erratically in the same manner, an effect which appears to originate from lack of uniform packing of the pads. Large corrections for capillary electro-osmosis have been found necessary, and the ratio of the ζ-potential, calculated from electro-osmosis, to that from the stream potential was greater than unity, and increased with increase in pad concentration.   H. H. H.

Electrokinetic Properties of Cellulose Fibres. II— Zeta-potential Measurements by the Stream-Compression Method. D. A. I. Goring and S. G. Mason. *Canadian J. Res.*, B 28, 323–338 (June 1950).

A new technique of measuring the ζ-potential of cellulose fibres is described, in which stream current and stream potential measurements are carried out over a range of solid concentrations on a single pad. In this method, it is necessary to measure the D.C. resistance of the pad, since a pronounced dispersion effect yields A.C. resistance values of considerable error, and reversible electrodes are used whereby stream current measurements can be made. Degrees of swelling, calculated from the stream data, are consistently higher than those calculated from permeability measurements, and the discrepancy indicates a serious limitation of the conventional electrokinetic theory when applied to swollen cellulose. A model of the fibre-liquid interface, consisting of partly dissolved electrically charged cellulose chains accounting for the observed discrepancy, is discussed, and, if this model is applicable, the physical significance of the ζ-potential appears extremely complex.   H. H. H.

Electrokinetic Properties of Cellulose Fibres. III— Note on the Low Frequency Dispersion of Electrical Resistance. D. A. I. Goring, G. J. Biefer, and S. G. Mason. *Canadian J. Res.*, B 28, 339–344 (June 1950).

Sulphite cellulose, rayon cellulose, and silk fibres in the presence of 10^{-4} N-KCl show a 20–25% decrease in electrical resistance between 0 and 100 cycles/sec., and an additional but smaller decrease between 100 and 15,000 cycles/sec.; the systems also show a marked capacitive reactance. Reversal of the sign of the ζ-potential in sulphite fibres destroys the effect. Non-swelling fibres such as asbestos, glass, and acetate rayon, slightly swelling nylon, and moderately swelling wool show no comparable behaviour. It cannot yet be concluded whether the phenomenon is associated with the surface or the interior of the swollen fibres.   H. H. H.

Chemical Delignification of Flax. E. Besser, R. E. Montonna, and F. Smith. *Nature*, 166, 195–196 (29th July 1950).

Seed flax straw in which lignification has proceeded to completion is treated for 2 hr. at 155°c. under pressure with an aq. soln. containing 2% sodium hydrosulphite and 2% sodium hydroxide, resulting in complete delignification while leaving cellulose fibres which are readily spun into yarn. It is possible to separate the constituents, e.g. cellulose, lignin, hemicellulose, and pectic acid, from flax straw. The method is applicable to grains, leaves, straws, and some types of wood.   J. W. B.

Studies on Manilla Hemp. I— Chemical Composition. K. Atsuki and S. Matsumura. *J. Soc. Textile Cellulose Ind. Japan*, 1, 642–645 (1945): *Chem. Abs.*, 44, 5596 (25th June 1950).

Manilla hemp is composed of practically pure lignin cellulose, the pectin content determined by the calcium picrate method being only 0·43–0·52%. The lignin is formed from a vanillin nucleus. The X-ray refraction pattern shows the pentosan to be adsorbed on the surface of the cellulose micelle. Softening of hemp is best done by removal of the lignin.   C. O. C.

Fine Structure of Silk Fibroin. R. Hegetschweiler. *Makromol. Chem.*, **4**, 156–183 (1949): *Chem. Abs.*, **44**, 5682 (10th July 1950).

Studies of double refraction by immersion and imbibition methods gave consistent results. Values of n_D^{19} were 1·5690 parallel, and 1·5454 perpendicular, to the fibre axis. Contrary to Ohara's conclusions (*Chem. Abs.*, **27**, 3614 (1933)) no evidence was found for dependence of the double refraction of the fibre on the refraction of the imbibition medium in the sense of a rod double refraction effect. Variations in optical anisotropy were explained on the basis of swelling. The electron microscope showed the presence of densely packed fibrils varying from 10 to 100 mμ. in diameter. There are 30 references.   C. O. C.

Crystallisation of Fibroin. S. N. Beketovsky. *Tekstil. Prom.*, **10**, 35 (May 1950).

Degummed silk is dispersed at a concn. of 100 g. per litre in a 40% soln. of lithium nitrate at the boil. From the sol, after filtration and dialysis, fibroin crystallises out in small needles.   A. E. S.

Physicochemical Studies on Manufacture of Artificial Fibres.— I–VIII. H. Malda. *J. Soc. Textile Cellulose Ind. Japan*, **1**, 651–654, 654–658, 669–672, 672–677 (1945); **2**, 8–13, 13–19, 53–55, 56–58 (1946): *Chem. Abs.*, **44**, 6115–6116 (10th July 1950).

I— Quantitative Observation of Crystalline Region of Cellulose. *Ibid.*, **1**, 651–654 (1945).

Heating mercerised cotton or cellulosic rayon with 1–4% H_2SO_4 hydrolysed the non-crystalline cellulose to compounds of lower mol. wt. which broke away from the C chains and were easily removed with 1% NaOH. From the yield and viscosity of the residual crystalline portion, the distribution of the crystalline and non-crystalline parts and the length of the crystalline particles were estimated.

II— Evaluation of the Determination of the Crystalline Region. *Ibid.*, **1**, 654–658 (1945).

Compared with the original fibres the crystalline part separated above was less hygroscopic, had lower affinity for dyes, linked less with saturated acetic acid, had greater sp. gr., and gave an almost heterogeneous equilibrium curve with NaOH, showing that the non-crystalline part had been almost completely removed.

III— Crystalline and Non-crystalline Regions of Natural Cellulosic Fibres. *Ibid.*, **1**, 669–672 (1945).

The above method was used to compare the microstructures of ramie, cotton, and conifer, broadleaf, and ricestraw pulps. Pentosan was almost all found in the non-crystalline region (between the micelles) in the wood pulps but in the crystalline part in the straw pulp.

IV— Alkali Immersion and Aging of Cellulose. *Ibid.*, **1**, 672–677 (1945).

When immersed in NaOH the crystalline particles, although linked through the main C chain, acted as particles of an independent component and phase (different energy level), and the crystalline region gradually changed to the non-crystalline region. On aging in NaOH breakaway by oxidative decomposition occurred only in the non-crystalline region.

V— Sulphonation and Solution of Xanthated Cellulose. *Ibid.*, **2**, 8–13 (1946).

Sulphonation occurred first in the non-crystalline region and then on the terminals and surface of crystalline particles in the crystalline region, to proceed gradually into the interior, some sulphonated parts here shifting into the non-crystalline state of greater entropy to dissolve and disperse and simultaneously to promote diffusion of CS_2 into the interior for further sulphonation. Easy solution of xanthated cellulose was explained by formation of a hydrophilic layer by xanthate ions by fixing the H_2O mol. (in NaOH solution) and thereby weakening the secondary covalence between the main chain atoms.

VI— Dispersed State of Viscose and its Change during the Heat Finishing Process. *Ibid.*, **2**, 13–19 (1946).

Much of the cellulose in viscose is dispersed in the mol. unit, the mol. forming a thread rolled up into a ball. However, a small area may remain in the primary crystalline state. During heat finishing the crystalline region was disintegrated first and resurrected later.

VII— Physicochemical Changes during Coagulation of Viscose. *Ibid.*, **2**, 53–55 (1946).

From 1% viscose coagulated in H_2SO_4 with or without adding Na_2SO_4, $PbSO_4$, or NaOH, coagulation started on the surface adjacent to the bath wall and proceeded inward.

**VIII— Crystallisation of Cellulose in Spinning Viscose.** *Ibid.*, **2**, 56–58 (1946).

Data giving information about the amount of crystallinity occurring in viscose rayon and its relation to the speed and conditions of spinning.   C. O. C.

Solubility of Cellulose in a 10% Solution of Caustic Soda. A. Pakshver and S. Florov. *J. Appl. Chem. (U.S.S.R.)*, **23**, 530–535 (May 1950).
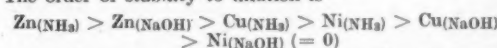
The solubility of regenerated cellulose (viscose or cuprammonium rayon) in a 10% soln. of caustic soda is found to vary considerably according to the physical condition of the preparation. Thus, viscose fibre, when introduced into the caustic soda soln. in the wet condition, dissolves to a much greater extent than when it is treated after drying, while, in either case, the application of tension to the fibre (while wet and, in the second case, during drying) reduces the solubility figure. This figure is regarded as a measure of the effectiveness of the intermolecular linking, and this, in its turn, depends on the length of the cellulose molecules and their disposition. Drying, particularly under tension, results in increased cross-linking, which is sufficiently stable to withstand the prolonged action of 10% caustic soda soln. Electrolytes, which have a dehydrating effect on cellulose, act in an analogous manner. A 3% soln. of caustic soda appears to act essentially as an electrolyte, and viscose rayon treated with this soln. is of low solubility in 10% caustic soda. Further results, consistent with the above views, are given for cellulose regenerated from cuprammonium soln. Rayons are examined at various stages of the commercial process. Also, preparations obtained by pouring a cuprammonium soln. of cellulose into a soln. of sulphuric acid or ammonium sulphate are examined at various times after precipitation. The newly formed cellulose is of high solubility, but as orientation and cross-linking processes proceed, the solubility falls. With sulphuric acid as coagulant the solubility ultimately rises again, owing to a reduction in chain length produced by hydrolysis. The effect of the age of the spinning soln. is considered, and it is found that the degradation occurring during ageing is reflected in the solubility figure of the coagulum.   A. E. S.

Solubilities of the Hydroxides of Copper, Zinc, Nickel, and Cobalt in Solutions of Caustic Soda and Ammonia. [Dissolution of Cellulose in Alkaline Solutions of Metal Hydroxides.] M. I. Arkhipov, A. B. Pakshver, and N. I. Podbornova. *J. Appl. Chem. (U.S.S.R.)*, **23**, 650–656 (June 1950).

The two main factors favouring the dissolution of cellulose in alkaline solutions of metal hydroxides have been shown previously (cf. J.S.D.C., **66**, 389 (July 1950)) to be— (1) The formation of a complex compound between the metal hydroxide and NaOH or NH_3, and the solubility of this compound. (2) The instability of this compound when brought under the influence of the OH groups of cellulose. The solubility of the metal hydroxide in the alkaline soln. is taken as a measure of the first factor, while the instability of the complex metal hydroxide soln. to dilution by water is considered to be in some degree related to the second. These two properties are measured for solutions of $Cu(OH)_2$, $Zn(OH)_2$, and $Co(OH)_2$ in aq. NaOH, and $Cu(OH)_2$, $Ni(OH)_2$, and $Zn(OH)_2$ in aq. NH_3. The order found for the solubility of the hydroxides is—

$$Zn_{(NaOH)} > Zn_{(NH_3)} > Cu_{(NH_3)} > Ni_{(NH_3)} > Cu_{(NaOH)} > Co_{(NaOH)} > Ni_{(NaOH)} \ (= 0)$$
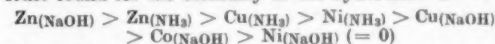
The order of stability to dilution is—

$$Zn_{(NH_3)} > Zn_{(NaOH)} > Cu_{(NH_3)} > Ni_{(NH_3)} > Cu_{(NaOH)} > Ni_{(NaOH)} \ (= 0)$$

($Co(OH)_2$ was not investigated). The solubility of cellulose in these solutions is shown to be in general agreement with the view that the measured properties are major determining factors. In particular, the inability of ammoniacal $Zn(OH)_2$ to dissolve cellulose is attributed to the exceptionally high stability of the complexes present. It is considered, however, that, in general, there are other contributing factors which require study.   A. E. S.

Swelling and Shrinkage of Artificial Cellulosic Filaments and of Yarns and Fabrics made from them. F. Girard. *Bull. Inst. textile France*, No. 9, 37–52 (1949): *Chem. Abs.*, 44, 5597 (25th June 1950).

Natural and artificial cellulosic fibres or filaments, whether untreated or treated to lower their water-absorptive properties, show diametrical and longitudinal swelling and volume increase proportional to absorbed water content after centrifuging. Diametrical swelling is approx. 30% for untreated artificial cellulosic filaments, 14% for treated filaments, and 13% for cotton fibres. The longitudinal increase of the fibres is lost on drying. Yarns show diametrical swelling proportional to, but smaller than, that of the constituent filaments or fibres. This swelling combined with torsional effects of spinning results in longitudinal shrinkage of the yarn; this shrinkage is partly recoverable by drying and reoccurs on subsequent rewetting. The same effect is noticeable in fabrics woven from these yarns.   C. O. C.

Synthetic Fibres made from Proteins. H. P. Lundgren. *Advances in Protein Chemistry*, 5, 1–82 (1949).

Vicara. P. A. Koch. *Textil-Rund.*, 5, 278–280 (July 1950); *Deutsche Textilgewerbe*, 52, 177–178 (1950).

The chemical composition, physical and chemical properties, and preparation of Vicara, a protein fibre from maize, are tabulated. It is recommended for use with cotton, spun rayon, wool, and polyamide fibres as a mixed fibre for the production of underwear, knitted goods, and hosiery.   B. K.

Pilot-plant Operation for making Gosei-Ichigo (i.e. Synthesis No. 1) Fibre from Polyvinyl Alcohol. S. Lee. *Chem. High Polymers* (Japan), 2, 179–195 (1945).

<div align="center">PATENTS</div>

Preventing Formation of Rock-like Deposits on Thread Guides, Godets, or Thread-advancing Reels during Production of Viscose Rayon. Courtaulds Ltd. and J. Wharton.   B.P. 640,105.

Aftertreatment of Regenerated Cellulose Products. A. Politzer and Oscar Kohorn & Co. Ltd.
B.P. 2,501,090.

Regenerated cellulose filaments, foil, etc., after being desulphurised, are washed with water until the effluent has pH 9·5–10·5. The material is then washed with a 0·05–0·1% solution of a complex-forming phosphate, after which it is rinsed and processed as usual. This treatment is quicker and cheaper, and results in a better product, than the usual acid treatment.   C. O. C.

Staple Fibres of Organic Derivatives of Cellulose produced by Solvent Dyeing, Mechanical Crimping, and Cutting in that order. C. M. Croft and Celanese Corpn. of America.   U.S.P. 2,504,183.

Resin-treated Regenerated Protein Fibres. J. J. Press.   B.P. 638,356.

The tensile strength of regenerated protein fibres is improved by impregnating the freshly prepared stretched fibre with a mixture of condensable bodies, e.g. urea and formaldehyde, at a pH below the isoelectric point of the protein and drying at < 70°c.   W. G. C.

Resists on Polyamides and Increasing the Fastness of Dyed or Printed Polyamides. Sandoz Ltd.
B.P. 640,421.

Polyamides which have been treated with colourless thio derivatives of phenols, preferably in aqueous alkaline solution at 60–100°c., are rendered resistant to direct, acid, sulphur, chrome, and vat dyes. Alternatively dyed or printed polyamides treated in this manner show increased fastness, especially to water, acids, perspiration, and cross-dyeing, without any decrease in fastness to light. C. O. C.

Solutions of Acrylonitrile Polymers containing a Colourless Acidic Compound. R. A. Scheiderbauer and Du Pont.   U.S.P. 2,502,030.

Incorporation of a chemical compound which will react with amines into dimethylformamide solutions of acrylonitrile polymers permits prolonged standing of the solutions or exposure to high temperature for lengthy periods without much discoloration.   C. O. C.

Solutions of Acrylonitrile Polymers and Fibres from them. H. W. Coover, T. E. Stanin, J. B. Dickey, and Eastman Kodak Co.   U.S.P. 2,503,244.

Clear, colourless, and gel-free solutions of acrylonitrile polymers are obtained by mixing the polymers with *NN*-dimethylformamide or *NN*-dimethylacetamide in presence of an oxy acid of phosphorus or its anhydride. Fibres spun from such solvents are lustrous, white, and of uniform strength or tenacity.

U.S.P. 2,503,245.

The phosphorus acids may be replaced by oxalic, acetic, or trifluoroacetic acid or by an alkanesulphonic, aromatic sulphonic, alkylphosphoric or alkylphosphorous, alkylphosphonic, or alkenesulphonic acid.   C. O. C.

Monofilaments resembling Yarns. H. Wurzburger.
B.P. 640,386.

Monofilaments of a homogenous organic plastic material are embossed so that they have an open groove or several parallel grooves on their surface, these grooves being at an angle to the axis of the filament, so that they not only give the appearance of twisted filaments but also impart flexibility to the monofilament.   C. O. C.

Non-woven Fabrics. Courtaulds Ltd., J. H. Macgregor, and F. Happy.   B.P. 640,411.

A layer of fibres consisting wholly or partly of cyanoethylated cellulose (prepared by etherifying cellulose with acrylonitrile while maintaining its fibrous structure) is treated so as to render the cyanoethylated cellulose adhesive and thus cause bonding of the fibres, e.g. by treatment with suitable solvents with simultaneous or subsequent application of pressure.   C. O. C.

Cellulose Esters insoluble in Organic Solvents. H. J. Hagemeyer and Eastman Kodak Co. (X, p. 567.)

Improving the Resistance to Heat of Nylon. I.C.I. Ltd. (X, p. 567.)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Washing as a Wetting Process. W. Kling. *Kolloid-Z.*, 115, 37–44 (Oct.–Dec. 1949).

By means of oil for the simulation of dirt, a satisfactory theoretical and experimental investigation of the washing process has been carried out, which establishes the latter as a wetting-out mechanism. A quantitative treatment, however, is not yet possible.   H. H. H.

Scouring with Synthetic Detergents. Anon. *Dyer*, 104, 91–94 (28th July 1950).

Although synthetic detergents, e.g. Lensex and Lissapol N, are, in many respects, superior to soap in scouring raw wool and wool yarn, a disadvantage is that their effluents are not so readily cracked in sewage treatment. The disposal of sewage containing synthetic detergents is discussed. Whilst there is some evidence that their presence in quantity would cause no serious consequences, it is considered that further collaboration between wool scourers, detergent manufacturers, and sewage authorities is required to solve the problems involved.   W. K. R.

Comparative Detergency of Surface-active Agents on Woollen Cloth. K. S. La Fleur. *Amer. Dyestuff Rep.*, 39, 385–388 (12th June 1950).

Results are tabulated of a comparison of the efficiency, on an equal concentration and an equal cost basis, of 28 detergents representing distinct chemical types, in removing a self-emulsifying mineral oil from woollen cloth. Laboratory trials were carried out at 100°F. and 10 : 1 liquor ratio using each detergent alone and together with a neutral (NaCl) and an alkaline (Na_2CO_3) builder. The most efficient product, on either basis, was a polyoxyethylene thioether (I) used with NaCl, and an alkarylpolyoxyethylene condensate (II) was second best. Almost all the other detergents were inferior to soap on a cost basis. Owing to the poor solubility of I, a mixture of equal parts of I and II was considered to be the most effective detergent for practical use, optimum scouring conditions being 0·5% of the mixed detergent and 4% NaCl on the wt. of the cloth. The findings were confirmed by limited mill trials.   W. K. R.

Modern Trends in the Use of Detergents. P. B. Law. *Textile J. of Australia*, 25, 189–192 (April 1950).

The functions of a detergent are outlined under the headings— wetting, absorption, emulsification, soil dispersion, and prevention of redeposition. Some experiments are described which illustrate the value of small amounts of carboxymethyl cellulose in reducing soil redeposition with detergents of various types, including soap.

　　　　　　　　　　　　　　　　　　W. K. R.

Some Aspects of Chlorine Retention by Resin-treated Fabrics. A. C. Nuessle and J. J. Bernard. *Amer. Dyestuff Rep.*, 39, P 396–P 403 (12th June 1950).

Fabrics containing nitrogenous resins retain chlorine when bleached with hypochlorites. In a study of the effect of bleaching conditions on the chlorine retention, colour change, and strength loss of resin-treated viscose rayon, it was found that small amounts (< 0.4% approx.) of retained chlorine are harmless, but larger amounts cause loss of strength on subsequent ironing. The quantity of residual chlorine was chiefly influenced by the available chlorine content and the liquor : goods ratio of the bleaching bath. Fabrics containing urea resins showed loss of strength at lower chlorine retentions than fabrics treated with melamine resins, though only the latter developed a yellow colour during bleaching. One type of resin treatment, a modified urea–formaldehyde, retained only small amounts of chlorine under all conditions, and consequently suffered no appreciable yellowing or strength loss. Factors influencing to a lesser extent chlorine retention and damage included concentration of resin, duration and temp. of bleaching and rinsing, and temp. of subsequent ironing. A number of methods for determining retained chlorine were compared.　　　　　　　　　　W. K. R..

PATENTS

Removing Oil from Carded Webs, Batts, or Thin or Knitted Fabrics. G. H. Wood, C. S. Francis, and Felters Co. Inc.　　　　　　　　　　U.S.P. 2,501,979.

The material is quickly freed from oil by treating it with a current of hot air so as to volatilise the oil. Apparatus for treating batts for felt is described.　　　C. O. C.

Activating the Oxidising Power of Chlorite Solutions and Bleaching Cellulosic Material therewith. Solvay & Cie.　　　　　　　　　　B.P. 640,394.

A chlorite solution used for bleaching cellulose may be activated by contact with a multivalent metal, e.g. Cr, Fe, Co, Ni, Cu, or Mn, or an alloy or an insoluble compound of such a metal, the degree of activation being regulated by varying the extent and/or the duration of the contact, according as the solution is at rest or in motion. When the solution is used in metal vessels they are polarised to prevent their causing uncontrollable activation. C. O. C.

Decolorising Polyvinyl Halides or their Copolymers. N. V. Philips' Gloeilampenfabrieken.　　B.P. 640,460.

Better and frequently more rapid bleaching is obtained by treating the swollen material with hydrogen peroxide instead of the usual chlorine or chlorine dioxide. C. O. C.

Studies in Detergency. VIII— Electron-microscopic Observations of Fibre Surfaces. W. Kling and H. Mahl. (VI, p. 562.)

VIII— DYEING

Some Applications of Modern Microscopy to the Study of Chemical Phenomena and in the Dyeing and Printing of Textiles. G. L. Royer. *A.S.T.M. Bulletin*, No. 165, 47–48 (April 1950).

Modern microscopical equipment and technique are described briefly, and some instances are listed of the use of microscopy in textile printing, dyeing, and finishing investigations.　　　　　　　　　　W. K. R.

Studies on Foams. III— Foam Formation of some Dye Solutions. M. Nakagaki. *Bull. Chem. Soc. Japan*, 22, (5), 200–203 (1949).

Foam formations and surface activities of six aqueous dye solutions are correlated, the relation being explained in terms of the structural formulæ of the dyes. J. W. B.

Influence of Temperature on the Absorption of Acid and Direct Dyes by Wool, Silk, and Ardil. E. Elöd and H. G. Fröhlich. *Melliana Textilber.*, 31, 335–337 (May 1950).

The absorption of various acid and direct dyes on wool, silk, and Ardil is plotted as a function of temperature. With acid dyes on silk there is considerable absorption in the cold and only slowly increasing absorption with increase in temperature. On wool, however, the acid dyes give only low absorption in the cold and rapidly increasing absorption in the region of 50°c. Ardil behaves qualitatively like wool, but gives somewhat higher absorption at all temperatures. The absorption of direct dyes increases rapidly at about 40°c. on silk, at 60–70°c. on wool, and at an intermediate temperature on Ardil. All three fibres were found to show a swelling of about 50% under the conditions of the dyeing experiments, so that differences in swelling do not account for the differences in dyeing behaviour. A part explanation is the presence on the wool fibre of an outer layer which hinders access of dye at low temperatures, but Ardil, which does not possess such an outer layer, behaves in a somewhat similar manner to wool. It is concluded that the ratio of polar to non-polar groups in the fibre has an influence on dye absorption. Wool and Ardil, which are more polar than silk, are not so easily penetrated by dyes. Differences in the fastness properties of the dyes on the various fibres are also ascribed to differences in the ratio of polar to non-polar groups in the fibres.　　　　　　　　　　F. A.

Survey of Recent Developments in the Wet Processing of Full-fashioned Hosiery. H. L. DeTurck. *Amer. Dyestuff Rep.*, 39, P 404–P 408 (12th June 1950).

Problems relating to the dyeing and finishing of nylon hose made from multifilament yarns together with 15-denier and 20-denier monofilament yarns are discussed, particularly the difficulty of obtaining an even shade on the two types of yarn. The results of experimental work carried out with the object of achieving a satisfactory union are described. The use of selected acetate dyes is considered to give the best, though not entirely satisfactory, results.　　　　　　　　　　W. K. R.

Researches on Vat Dyeing. R. Haller. *Helv. Chim. Acta*, 33, 1165–1171 (Aug. 1950).

Processes which occur during vat dyeing, e.g. of indigo, are investigated, and it is found that, whereas dispersion of indigotin does not take place, the vigorous conditions of the vat occasion some disintegration of the cotton fibre; the products indicate that a certain amount of hydrolysis has occurred. No satisfactory explanation can yet be given of dye penetration through the cell wall by the path of greatest resistance, nor for the circumstances of its subsequent crystallisation in the fibre.　　　　H. H. H.

Production of Chemically Dyed Fibre. Z. A. Rogovin, A. G. Yashunskaya, and B. M. Bogoslovsky. *J. Appl. Chem.* (*U.S.S.R.*), 23, 631–640 (June 1950).

Cellulosic fibres were treated with periodic acid so as to yield a dialdehydocellulose. This was then condensed with *p*-aminophenol or 2:8-aminonaphthol-6-sulphonic acid, and the resulting product was coupled with a diazonium salt. Yellow to brown dyeings were obtained. The coloration was of good fastness to washing, perspiration, and rubbing, and was not affected by pyridine, glacial acetic acid, or hot solutions of mineral acid. The light-fastness was not outstanding. Not more than 50% of the aldehyde groups of the dialdehydocellulose could be brought into reaction with the amine. This is considered to be related to the differing reactivities of the two aldehyde groups, one of which belongs to a glyoxal residue and the other to an erythrose residue. In order to obtain full shades 1–2% of the secondary alcohol groups of cellulose must be converted into aldehyde groups. In the case of cotton fabrics this process and the succeeding reactions lead to a considerable loss in tensile strength, and the method is of no practical value. In the case of viscose rayon there is, in general, no appreciable loss in strength in the series of reactions considered, but in a subsequent alkaline wash up to 20% loss in tensile strength may occur. This is considerably less than the loss suffered by the same fabric at the dialdehydocellulose stage, when submitted to the same

test. The loss in strength of the dyed material is attributed to the presence of uncondensed aldehyde groups, and may be prevented by blocking the latter by a treatment with hydroxylamine.   A. E. S.

Electrocolouring of Stainless Steels in Aqueous Solutions. C. E. Naylor. *Australia, Dept. Supply & Development, Plating Notes*, 1, 2–14 (1949).

Chemical Fundamentals of Wood Staining. W. Kesting. *Farben, Lacke, Anstrichstoffe*, 4, 82–84 (1950): *Chem. Abs.*, 44, 5611 (25th June 1950).

Basic dyes are absorbed four times as much as acid dyes by wood, but they tend to bleed into lacquer finishes. Alcoholic dye solutions penetrate better than aqueous solutions, and do not roughen the wood as much. The best stains are obtained by producing the colour within the wood by the use of metal salts (Cr, Cu, Fe, Ni, Co, Mn, Sb, V, Al), alkalis (NaOH, KOH, $Ca(OH)_2$), and tannins, polyphenols, or aromatic amines. In some cases, aftertreatment with ammonia produces patina and antique effects. Oxidants, e.g. H_2O_2 or $Na_2Cr_2O_7$, often suffice to produce a stain with the tannins or with the mordant. C. O. C.

PATENTS

Dyeing with Acid Dyes. Wolsey Ltd., P. Alexander, and D. A. Charman.   *B.P.* 640,419.

Wool or other fibres having affinity for acid dyes are immersed for a short time in a solution of a surface-active acid dye at not > 50°c., being taken out of the solution before the bath is exhausted; after removal of excess liquor, the dye is fixed on the fibres either by drying or exposure to steam at > 40°c., preferably by steaming at 90–140°c. This method gives level dyeings with all types of acid dyes, can be applied as a continuous process, avoids weakening of the material being dyed, and is much more economical in fuel than the usual acid dyeing methods.
                                              C. O. C.

Dyeing Keratinous Fibres. E. B. Michaels, B. Berk, and Lawrence Richard Bruce Inc. *U.S.P.* 2,501,184.

Keratinous fibres, e.g. human hair, may be dyed at body temperature by using a liquor containing dil. acetic acid, urea, and dyes which normally have no affinity for the fibre, e.g. D&C Black No. 1, D&C Brown No. 1, and External D&C Red No. 13.   C. O. C.

Dyeing Cellulose Acetate Staple-fibre Fabrics. British Celanese Ltd.   *B.P.* 639,885.

Mottled effects are avoided by using a solution of the dye in ethyl alcohol of not < 94% strength by weight. The ethyl alcohol may be wholly or partly replaced by other lower aliphatic alcohols.   C. O. C.

Dyeing Cellulose Acetate with Acid Dyes. American Viscose Corpn.   *B.P.* 640,458.

When using alcoholic dyebaths or the "acid assistant" method (i.e. use of a mixture of organic and inorganic acids in the dyebath), addition to the aqueous solution of the acid dye of 1–6% (on the weight of the dyebath) of a hydroxy derivative of either benzene or a polyhydrobenzene, e.g. resorcinol, phloroglucinol, or *cyclo*hexanol, enables the concentration of alcohol or acid primary assistant in the bath to be drastically reduced without detriment to the resulting dyeings.   C. O. C.

Calculation of Steam Requirements in Winch Dyeing. E. Wachendorff. (I, p. 554.)

Electrokinetic Properties of Cellulose Fibres. I— Stream Potential and Electro-osmosis. D. A. I. Goring and S. G. Mason. (VI, p. 562.)

Electrokinetic Properties of Cellulose Fibres. II— Zeta-potential Measurements by the Stream– Compression Method. D. A. I. Goring and S. G. Mason. (VI, p. 562.)

Resists on Polyamides and Increasing the Fastness of Dyed Printed Polyamides. Sandoz Ltd. (VI, p. 564.,

Pigment Compositions for Decorative Textiles. S. Lee and Interchemical Corpn. (IX, this page.)

IX— PRINTING

Use of the Stroboscope on Printing Machines. B. Richter. *Melliand Textilber.*, 31, 424–426 (June 1950).

The flash frequency required for flicker-free observations on printing machines is given as a function of cloth speed and pattern repeat. Apparatus for controlling the frequency is described.   F. A.

Intensifying Action of Urea in Printing. R. Haller. *Melliand Textilber.*, 31, 349–351 (May 1950).

Urea does not act as an electrolyte in direct dyebaths, nor does it have any swelling action on cellulosic fibres even in hot conc. solution. It was thought that its intensifying action in the printing of direct and acid dyes on vegetable fibres might be due to increased dispersion of the dye. Experiments on the diffusion into gelatin and dialysis of direct dye solutions failed, however, to detect any increase in dispersion. Urea has a strong swelling action on starch, but its intensifying action is also observed when printing with tragacanth and gum arabic. The urea can be recovered unchanged from steamed prints. An explanation of its mode of action cannot yet be given.   F. A.

Squeegee Lifting Devices. R. Künzl. *Melliand Textilber.*, 31, 356–357 (May 1950).

Single-handed operation of a printing screen is made possible by using a double or a tilting squeegee. These methods, however, are not practicable with heavy fabrics, and are replaced by devices for lifting a heavy squeegee over the printing paste at the end of the frame. These devices, which consist of lifting pins on the squeegee and cams on the frame, are described and illustrated. F. A.

PATENTS

Hydroxylammonium Salts as Developers for Sulphuric Esters of Leuco Vat Dyes. H. L. Sanders and General Aniline & Film Corpn. *U.S.P.* 2,503,300.

Compounds of formula NH_3OHX ($X = Cl$, HSO_4, SCN, or other strong acid radical), e.g. hydroxylammonium sulphate, are of wider applicability than, and develop any sulphuric ester of a vat dye without the discrimination characteristic of, the hitherto known developing agents. Thus employed in printing pastes they give excellent development of Algosol Golden Yellow IGK, Brown IBR, and Orange IRKL.   C. O. C.

Multicolour Printing of Fabrics composed of Fine Yarns. J. Forshaw.   *B.P.* 640,103.

Fine details of line and tone, such as cannot be obtained by any other known process, are produced in fabrics containing fine yarns, e.g. silk, by printing from a series of relief printing surfaces, e.g. plates, one for each colour, engraved, etched, or otherwise prepared for printing in relief except by use of the pin screen photogravure method.
                                              C. O. C.

Pigment Compositions for Decorative Textiles. S. Lee and Interchemical Corpn. *U.S.P.* 2,504,136.

The fastness to rubbing of fabrics dyed or printed with pigmented lacquers or aqueous emulsions of such lacquers is improved, without altering the handle of the material and with increase in the colour value obtained, by using a composition made up of a pigmented dispersion of a highmol.wt. solid thermoplastic monovinyl aromatic compound–conjugated diolefin copolymer and a volatile organic liquid.   C. O. C.

Diazotype Printing Materials. General Aniline & Film Corpn. and S. C. Slifkin.   *B.P.* 640,025.

A base coated with a mixture of > 3·7 g.-mol. of diazo compound and 1·0 g.-mol. of a dihydroxynaphthalene compound, capable of alkaline coupling to form mono- and poly-azo dyes, yields two-colour prints on white when dry-developed. Thus 2:3-dihydroxynaphthalene and the zinc chloride double salt of the diazo compound of 4'-amino-2':5'-dimethoxybenzanilide yield a green full-tone and a violet half-tone on a white background. C. O. C.

Diazotype Material comprising Amine Salts of Sulphonic Acid Azo Coupling Components. General Aniline & Film Corpn., W. H. von Glahn, L. N. Stanley, and M. A. Hand.   *B.P.* 640,491.

A diazotype material comprises a light-sensitive diazo compound suitable for two-component diazotypes, an azo dye coupling component containing at least one sulpho group, and an amine or a heterocyclic nitrogenous base

forming a salt with the sulpho group. The resulting prints are of improved fastness to washing.   C. O. C.

Change of Hue of Diazotype Images by Treatment with Moist Sulphur Dioxide Fumes. S. C. Slifkin and General Aniline & Film Corpn. *U.S.P.* 2,500,096.

Blue diazotype images, obtained by coupling a *p*-amino-benzenediazo compound, whose amino group is substituted at least once with an alkyl group, with the sodium salt of 2-naphthol-3:6-disulphonic acid, are turned to brown or sepia by exposure to the moist vapours of sulphur dioxide. They are reconverted to blue by treatment with an alkali, e.g. gaseous ammonia. The blue images are used for single copies and the brown or sepia images, with their high opacity to ultra-violet radiation, for producing transparent intermediate copies.   C. O. C.

Photographs on Textiles. J. Holden. *B.P.* 640,308.

The textile material is coated or impregnated with light-sensitive material and is temporarily stiffened by sizing before exposure, so that it is easily held flat while being exposed to light through a negative or transparency, the size being removed so as to restore normal handle of the material after formation of the photographic prints.   C. O. C.

Cleaning Azo-printed Regenerated Cellulose Gel with Hydrated Alumina. E. L. Wolfram.   *U.S.P.* 2,502,911.

Regenerated cellulosic material that has been printed in the gel state by developing an azo dye on it is cleared of excess developer by treating it while still in the gel state with an aqueous solution of an aluminium salt at a pH insufficient to injure the cellulosic material but sufficient to produce an incipient precipitate of aluminium hydroxide in the solution.   C. O. C.

Printing on Polyethylene. W. F. Henderson and Visking Corpn.   *U.S.P.* 2,502,841.

Polyethylene film can be printed if it is first treated with gaseous chlorine to such an extent that its transparency is not affected.   C. O. C.

Light-sensitive Anthraquinonesulphonic Acid Photo-printing Material containing a Cupric Salt. A. Schoen and General Aniline & Film Corpn.   *U.S.P.* 2,504,593.

Cupric salts are easily reduced to the cuprous state when exposed to light in presence of a light-sensitive anthra-quinonesulphonic acid or its alkali-metal salt, e.g. sodium anthraquinone-2:6-disulphonate, and the cuprous salts formed are readily converted into red to brown metallic copper images by heating to not < 100°c.   C. O. C.

Four-component Subtractive Colour Reproduction Process. J. A. Ball.   *U.S.P.* 2,507,494.

Five-component Subtractive Colour Reproduction Process. J. A. Ball.   *U.S.P.* 2,508,213.

Resists on Polyamides and Increasing the Fastness of Dyed or Printed Polyamides. Sandoz Ltd. (VI, p. 564.)

X— SIZING AND FINISHING

Influence of Lubrication on the Felting of Wool. R. V. Peryman and J. B. Speakman. *J. Textile Inst.*, 41, T 241–T 242 (June 1950).

It is found that wool flannel patterns, extracted with alcohol and ether, will shrink to only a small extent when hand-milled, using rubber gloves, over a pH range of 9·0–1·1. If small amounts of lubricant, e.g. oleic acid, are added to the wool from ethereal solution the samples shrink in the usual fashion when milled. It is concluded that residual oil and soap left in pieces that are to be acid-milled play an important part in controlling shrinkage rate.   J. W. B.

Modification Reaction of Wool Keratin. I. A. Shikanova. *J. Appl. Chem. (U.S.S.R.)*, 23, 667–672 (June 1950).

Evidence is advanced in support of the idea that the reaction of keratin with a polymethylene dihalide in presence of a reducing agent leads to the conversion of the cystine cross-link

$$-CH_2 \cdot S \cdot S \cdot CH_2- \text{ into } -CH_2 \cdot S \cdot [CH_2]_n \cdot S \cdot CH_2-$$

Cystine itself was treated in alkaline soln. with sodium formaldehyde-sulphoxylate and ethylene dibromide or 1-chloro-3-bromopropane, the conditions of the reaction

being very close to those necessary for the treatment of keratin. The expected products, containing interposed dimethylene and trimethylene respectively, were separated and identified by analysis and, in the case of the first compound, by chromatographic comparison with material synthesised by another method. Human hair keratin was then treated with sodium formaldehyde-sulphoxylate and ethylene dibromide. From the hydrolysate of this product a substance was isolated which was shown, by means of partition chromatography on paper, to be identical with the substance obtained from cystine and ethylene dibromide. It was free from cystine or other amino acid.   A. E. S.

Field Tests of Clothing treated to repel American Dog Ticks. P. Granett and C. F. French. *J. Econ. Entomol.*, 43, 41–44 (1950): *Chem. Abs.*, 44, 6072 (10th July 1950).

A method of testing repellents for *Amblyomma americanum*, by using trousers impregnated from the knee downwards, is described. Dibutyl adipate and *n*-hexyl mandelate, 2 g./sq. ft., from acetone solution or aqueous emulsion, gave a high degree of protection for 2–4 hr., even when clothing had been impregnated 2 weeks before the trials. Indalone, dimethyl phthalate, and *n*-propyl adipate were less effective.   C. O. C.

PATENTS

Imparting Crease Resistance to Cotton Fabrics. W. R. MacIntyre and Joseph Bancroft & Sons Co.   *U.S.P.* 2,504,857.

The loss in strength usually associated with the crease-resisting of cotton is largely avoided by using an aqueous solution of 80–20% of a di-, tri-, or tetra-methylol-melamine and 20–80% of a methylated methylolmelamine containing at least three hydroxymethyl groups, at least one of which is unmethylated and at least two of which are methylated. The weight of resins applied to the fabric is 3–20% on its dry weight.   C. O. C.

Straightening and Opening of Wool or Hair Pile. J. Caspé and American Cyanamid Co.   *U.S.P.* 2,501,435.

A fabric whose pile contains wool or hair is treated with formalin at pH 2–3 and then quickly treated with an iron roller at not < 350°F. so as to straighten, open, and soften the pile yarn. The pile is then treated with a solution of a heat-curable thermosetting aminoplast resin, and then again given a brief high-temperature ironing to cure the resin. The resultant pile is lustrous and water-repellent, and resembles the hair of a natural fur.   C. O. C.

Cellulose Esters insoluble in Organic Solvents. H. J. Hagemeyer and Eastman Kodak Co.   *U.S.P.* 2,500,029.

Acetoacetylation of partial esters or ethers of cellulose with diketen followed by treatment with formaldehyde yields products which are insoluble in organic solvents. The process may be applied during the production of filaments or may be applied to hydrolysed cellulose acetate textiles as a finishing process. The resultant filaments or textiles are resistant to moisture and wear, and do not swell in common organic solvents.   C. O. C.

Improving the Resistance to Heat of Nylon. I.C.I. Ltd.   *B.P.* 639,893.

Incorporation into nylon of a little of a hypophosphorous acid or a derivative of it gives increased resistance to loss of strength and discoloration on heating. Thus nylon textiles which have been impregnated with hypophos-phorous acid or a derivative and dried can be heat-set at > 140°c. but below the m.p. of nylon with but very little loss in strength and very slight discoloration.   C. O. C.

Permanent Water-repellent Finish. F. K. Signaigo and Du Pont.   *U.S.P.* 2,505,259.

A water-repellent finish fast to washing and dry cleaning is imparted to textiles by treatment with a soluble titanium compound, e.g. titanyl sulphate, and a long-chain (12–20 C) fatty acid ester of a polyhydric alcohol, the ester containing at least one alcoholic hydroxyl group and the alcohol being free from other reactive groups.   C. O. C.

Treating Textiles to render them more durable when Rubberised. M. R. Buffington and Lea Fabrics Inc.   *U.S.P.* 2,501,988.

Saturating textiles with a 2% solution of methyl cellulose and drying before rubberising results in products having improved durability.   C. O. C.

Coated Fabric. D. J. Sullivan and Du Pont.
U.S.P. 2,502,353.

Coated fabrics having excellent resistance to flexing and abrasion are obtained by using neoprene, acrylonitrile–butadiene copolymers, or other synthetic elastomers together with modified polyhydric alcohol–polybasic acid resins, the latter being formed *in situ* within the elastomer. These resins are obtained by condensing polyhydric alcohols with polybasic acids in presence of semi-drying oils or their acids and/or non-drying oils or their acids and/or natural acid resins as modifiers.   C. O. C.

Survey of Recent Developments in the Wet Processing of Full-fashioned Hosiery. H. L. DeTurck. (VIII, p. 565.)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

X-Ray Analysis of the Swelling of Wood Pulp in Sodium Hydroxide Solution. L. Jörgensen and E. Ribi. *Nature*, **166**, 148 (22nd July 1950).

Two pulps bleached with sodium chlorite are swelled at 3°c. in NaOH solutions of concentrations varying from 5·5 to 8·0% by wt., over which range sudden changes in the hydrolysis and water regains are observed. These properties are correlated with the transition from cellulose I to cellulose II as shown by X-ray diffraction data. The greater ease of mercerising wood pulps as compared with cotton and cotton linters is explained on the basis of difference in crystallite dimensions, while it is suggested that the transition is also dependent on the intercrystalline network.   J. W. B.

Preparations of Monocarboxycellulose. Z. Rogovin, L. Kondrashchuk, and R. Malakhov. *J. Appl. Chem.* (*U.S.S.R.*), **23**, 418–427 (April 1950).

A number of preparations of cellulose, in which the degree of polymerisation varied over a wide range, were oxidised by gaseous nitrogen dioxide so as to yield monocarboxycellulose of 3–4% carboxyl content (1 COOH to 6–8 glucose residues). In all cases the cuprammonium viscosity (1% soln.), initially ranging from 663 centipoises for raw cotton to 7 centipoises for viscose rayon, fell to a uniform value of 4·5–5·0 centipoises. Nevertheless, the tensile strength of the fibres was not reduced by the treatment, but when they were further treated in boiling water, a considerable reduction in tensile strength occurred, and the material was rapidly reduced to a powder. The conversion of the carboxyls into their calcium salts has no effect on this behaviour. The presence of the 6-COOH evidently leads to a reduction in the stability to hydrolysis of the adjacent glucoside link. This hydrolytic action occurs very rapidly in alkaline soln., even in the cold, and hence degradation occurs during the process of determining the cuprammonium viscosity or copper number. These properties cannot, therefore, be related to the degree of polymerisation of the original monocarboxycellulose. Monocarboxycellulose is insol. in conc. phosphoric acid, and the use of this solvent for viscosity determinations is therefore precluded also. The tensile strength of a monocarboxycellulose preparation is not affected by exposure in the dry condition to temperatures up to 130°c. Neither this treatment nor treatment in boiling water has any effect on the carboxyl content of the material.

The effect of the amount of moisture present during the preparation of monocarboxycellulose was investigated. Fabrics of bleached cotton, containing varying amounts of water, were treated to give a carboxyl content of 3–4%. It was found that under completely anhydrous conditions the tensile strength was reduced by about 35%. The presence of a very small amount of water led to a considerable increase in tensile strength, and for moisture contents of 3% and higher the tensile strength was greater than that of the original fabric (> 20% increase for 13% moisture). The treatment was, however, accompanied by a considerable fall in the resistance to repeated flexure, the number of flexions required for rupture being reduced more than a hundredfold for both cotton and viscose fabrics. It is considered that this effect can be explained in terms of the increase in lateral interaction between the

macromolecules following the introduction of carboxyl groups.

A comparison was made of the above 6-monocarboxycellulose with the dicarboxycellulose which is obtained from cellulose by the successive action of periodic acid and chlorous acid. In the latter the carboxyls arise from the oxidation of the 2- and 3-secondary alcohol groups with rupture of the pyranose ring. In each case cotton fabric was treated to give a carboxyl content of 2·8%, and no considerable loss in strength occurred. On boiling with water, the monocarboxycellulose fell to a powder, while the mechanical strength of the dicarboxycellulose was not affected appreciably. For comparison, the same fabric was treated with sodium hypochlorite soln. so as to yield a product with the same carboxyl content. In this case both primary and secondary alcohol groups are oxidised. The product is of reduced tensile strength, and suffers a considerable further loss in strength on boiling with water. It is emphasised that the position in the glucose residue at which oxidative attack occurs is of primary importance in determining the resulting degree of degradation of the cellulose.   A. E. S.

Comparative Study of the Conditions of Esterification and the Properties of Xylan and Cellulose. A. A. Konkin and Z. A. Rogovin. *J. Appl. Chem.* (*U.S.S.R.*), **23**, 536–544 (May 1950).

Xylan is compared with degraded hydrate cellulose preparations of about the same degree of polymerisation. It is found that xylan is more soluble than cellulose in dilute solutions of caustic alkali. Also, the rate of acetylation of xylan is greater than that of cellulose. Both facts are explained on the basis of the reduction of the intermolecular forces resulting from the absence of the primary alcohol side-group in xylan. The oxidation by the oxygen of the air of solutions of the polysaccharides in caustic soda soln. and in cuprammonium hydroxide soln. proceeds in much the same way for xylan and for cellulose, so that in this reaction the presence of a primary alcohol group in the molecule does not appear to be of considerable significance.   A. E. S.

Cellulosic Paper. Bakelite Corpn., H. W. Mackinney, and S. J. Schultz.   *B.P.* 639,884.

A heat-hardened condensate of urea (1 mol.) and formaldehyde (1·5–3 mol.) is modified by reaction at pH 2–12 with 2–20% by weight of its solids content of a polyhydric phenol, e.g. resorcinol, phloroglucinol, or pyrogallol, having at least two hydroxyl groups in the *meta* position to each other each having a hydrogen atom in the *ortho* position to it. The viscous resinous mass is dissolved in dilute aqueous alkali to give a sizing solution stable for several days. The sizing of the paper pulp suspension is carried out at pH 4–6 by adding sufficient acid to precipitate the resin on the pulp. The paper is then formed, and dried at an elevated temperature.   S. V. S.

Colour-stabilised Rosin Size for Paper. E. N. Poor, C. G. Landes, and American Cyanamid Co.
U.S.P. 2,502,884.

Incorporation of heat-treated tall oil pitch into pale or solvent-extracted wood or gum rosins prevents discoloration when paper sized with them is aged or heated.
U.S.P. 2,502,883.

The dark coloured substances removed from rosin by solvent purification are heated in an atmosphere free from oxygen for 1–3 hr. at 250–325°c. and used as the colour stabilisers. Alternatively, the rosin itself may be so treated and solvent purification omitted.   C. O. C.

Aftertreatment of Regenerated Cellulose Products. A. Politzer and Oscar Kohorn & Co. Ltd. (VI, p. 564.)

Production of Chemically Dyed Fibre. Z. A. Rogovin, A. G. Yashunskaya, and B. M. Bogoslovsky. (VIII, p. 565.)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Modification Reaction of Wool Keratin. I. A. Shikanova. (X, p. 567.)

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